MECHANISMS FOR THE HOMOGENEOUS, THERMAL CONVERSION OF METHANE TO ETHANE AND OTHER SATURATED HYDROCARBONS

PART 1

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MICROMEDIA

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INTRODUCTION

The objective of the present project was the investigation of a method for the thermal homogeneous conversion of methane into ethane and other higher hydrocarbons. The method evolved from studies of the thermal reactions of ethylene in the temperature region of 500°C (1) and the effect of small quantities of additives on the products of the chain reaction mechanism (2).

At 500°C ethylene reacts by a chain reaction mechanism, initiated by the bimolecular reaction of ethylene,

[1] $$2\,C_2H_4 \text{ -----> } C_2H_3 + C_2H_5$$

followed by addition, abstraction, decomposition and isomerization reactions of the ethyl, vinyl and higher radicals. The four major products, methane, ethane, propylene and 1-butene constitute about 80% of the products volatile at room temperature. Of these, methane and ethane are formed by hydrogen-abstraction by the corresponding radical, while propylene and 1-butene are formed by addition of radicals to ethylene followed by isomerization and decomposition of higher molecular weight radicals. Methane and ethane are the only saturated products, indicating first that methyl and ethyl radicals are major chain-propagating radicals, and second that only for methyl and ethly radicals is abstraction sufficiently fast to compete with addition.

Since the chain length is long and formation of products by termination may be neglected, the only important reactions giving methane and ethane are

[2] $$CH_3 + C_2H_4 \text{ ----> } CH_4 + C_2H_3$$

[3] $$C_2H_5 + C_2H_4 \text{ ----> } C_2H_6 + C_2H_3$$

In the presence of a small quantity of saturated hydrocarbon (3,4) the additional processes occur,

[4] $CH_3 + RH \longrightarrow CH_4 + R$

[5] $C_2H_5 + RH \longrightarrow C_2H_6 + R$

If the additive RH is stable at the temperature of the reaction and does not dissociate into radicals, no new initiation processes are introduced. If the quantity of additive is small, the general features of the chain mechanism are not altered and the main chain-carrying radicals and termination steps remain the same. Under these conditions the ratio of the rates of formation of methane and ethane in the presence and absence of the additive may be expressed as follows:

$$CH_4 \qquad \frac{(R^{\bullet}_{CH4})_a}{R^{\bullet}_{CH4}} = 1 + \frac{k_4[RH]}{k_2[C_2H_4]}$$

$$C_2H_6 \qquad \frac{(R^{\bullet}_{C2H6})_a}{R^{\bullet}_{C2H6}} = 1 + \frac{k_5[RH]}{k_3[C_2H_4]}$$

Results of studies using the additives ethane (3), propane and isobutane (4) and hydrogen (5) confirmed the validity of these equations and led to measurements of the ratios of rate constants applicable to the particular additive.

It is clear that in this system the additive RH was converted into methane and ethane and it follows that if the additive is methane it will be converted into ethane. In the presence of methane ethylene is therefore acting as a sensitizer for the decomposition of methane but with one important characteristic. In the ethylene reaction one of the main chain propogating radicals is the ethyl radical, which leads directly to ethane. Systems which sensitize the decomposition of methane but in which methyl is the dominant radical will be less efficient in conversion of methane to higher hydrocarbons.

The present study has investigated the kinetics of the formation of the major products, ethane, propylene and 1-butene in mixtures of ethylene and methane. The main problem was to find conditions of temperature, pressure and composition of the mixture where conversion of methane and ethane was a maximum. A high concentration of ethylene would maximize the over-all rate of the reaction, while a high concentration of methane would favor the conversion of methane into ethane. Conditions were sought to give the best balance of these effects.

Experiments were performed over the temperature range 500-580°C at pressures of ethylene from 12.5 to 200 Torr and ratios of methane/ethylene of 0 to 8.

EXPERIMENTAL

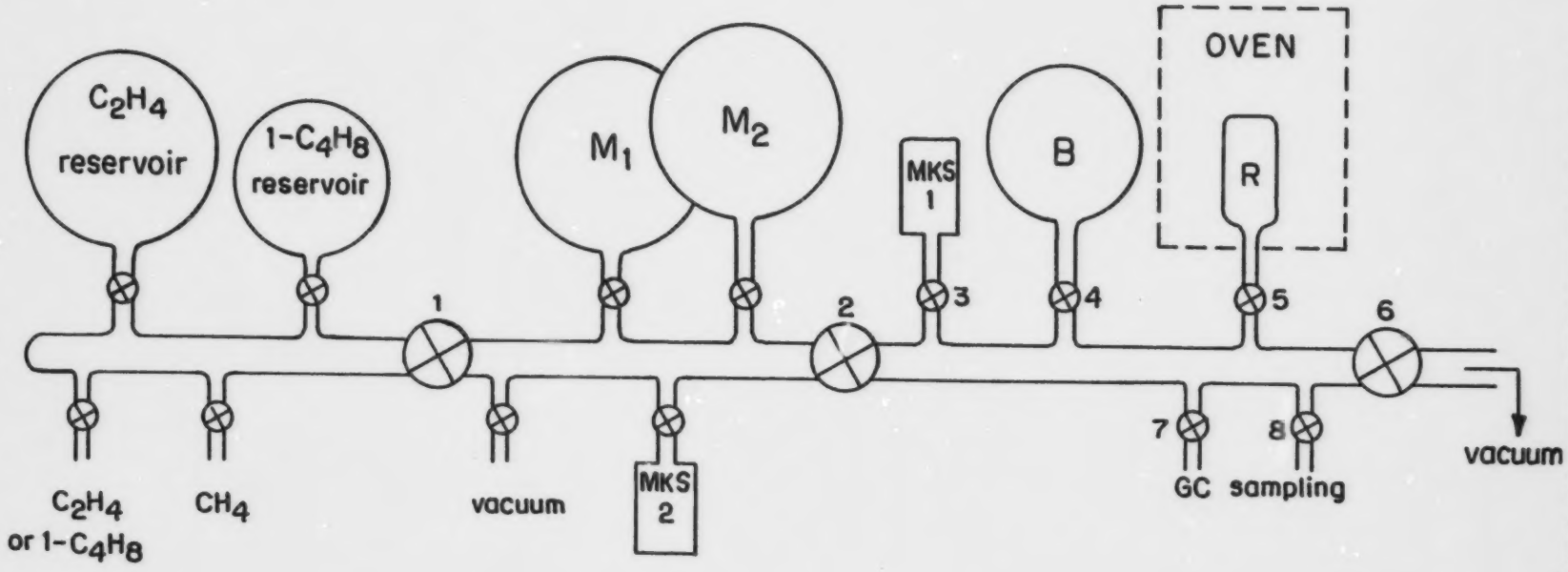
Apparatus

A classical static system has been used to perform the pyrolysis of the different mixtures. A diagram is shown in figure 1. The system was evacuated by two independent vacuum systems, each composed of a mechanical rotary pump and of a mercury diffusion pump. A vacuum of 10^{-5} Torr could be obtained. All stopcocks, made of pyrex, were greased with Apiezon N except for the reaction cell stopcock which was greased with Apiezon H, because of its proximity to the furnace. The 0.21 liter cylindrical reaction cell was made of quartz. A diagram of the cell and of its position in the furnace is shown in figure 2. The three zone furnace, Lindberg model #54457, was temperature controlled with a Lindberg, model #59744-A, control console. The temperature of the reaction cell, measured with a type K thermocouple, could be regulated within a $\pm 2^{\circ}C$ range.

The pressures were measured with two MKS Baratron absolute gauges, one, MKS 1, with a 0-1000 Torr pressure range and the other, MKS 2, with a 0-10 Torr pressure range.

Gases

Research grade ethylene (minimum purity 99.99%) and research grade 1-butene (minimum purity 99.9%) were obtained from Matheson Gas Products Canada. Both



M_1, M_2 : 5 liter mixing bulb

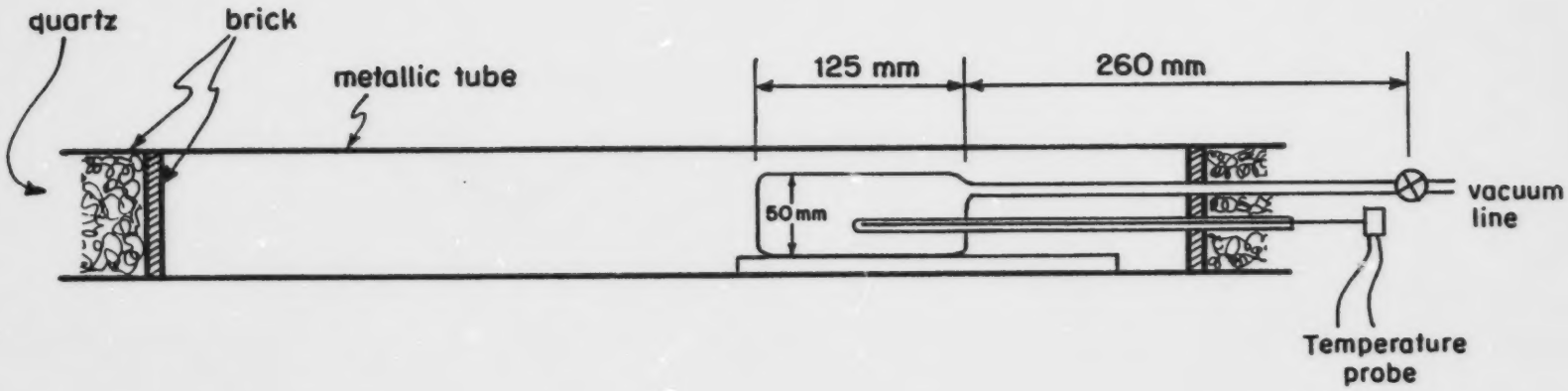
B : 2 liter balance volume

R : 0.21 liter quartz reaction cell

MKS 1 : 0 – 1000 Torr Baratron gauge

MKS 2 : 0 – 10 Torr Baratron gauge

FIGURE 1



scale 0.27

FIGURE 2

ethylene and 1-butene were submitted to a few freeze-pump-thaw cycles before they were stored for further use in 5 liter and 2 liter pyrex reservoirs. The main impurity remaining in ethylene was ethane and the main impurities remaining in 1-butene were ethane, ethylene and propylene. These impurities were too small ta affect the rates of formation of products, but corrections to the yields were made where necessary.

Research grade methane (minimum impurity 99.99%) was also obtained from Matheson Gas Products Canada and was used without further purification.

Experimental procedure

For each series of experiments, a mixture was prepared and stored in the five liter pyrex bulbs M_1 and/or M_2. This mixture was prepared by the following sequence:

1- ethylene and/or 1-butene, depending on the mixture studied, were submitted to a freeze-pump-thaw cycle to ensure that no air had leaked in their reservoir.

2- a calculated pressure of ethylene, or of 1-butene, was transfered from its reservoir to the mixing bulb M_1 and/or M_2 and this bulb was closed.

3- when 1-butene was used, the vacuum line was then filled with ethylene until the pressure reached a value higher (by a factor 3 or more) than the value of the pressure of 1-butene in the mixing bulb. The mixing bulb was then opened and ethylene allowed to fill the mixing bulb up to a calculated pressure.

4- methane was always introduced last in the same way as that described above.

5- once the mixture was made, it was allowed to stand in the mixing bulb for at least 1/2 hour before it was used. Experiments done after 1/2 hour or 24 or

more hours show no difference in their results, indicating that the mixing was completed after 1/2 hour.

Each experiment was done in the following way:

1- a calculated pressure of the mixture was transferred from the mixing bulb M_1 or M_2 to the 2 liter balance volume B and the stopcock #4 was closed.

2- the stopcock #2 was then closed and would remain in that position for the rest of the experiment. Stopcocks #5 and 6 were then opened in order to evacuate the reaction cell.

3- the experiment was started by closing the stopcock #6 and opening the stopcock #4. The stopcock #5 was then closed and the pressure read on MKS 1. The stopcock #4 was then closed again and the vacuum was made in the vacuum line.

4- during the pyrolysis, two 5 ml stainless steel sampling devices were attached to the vacuum line and were evacuated by opening the stopcocks #7 and 8.

5- at the end of the pyrolysis, the stopcock #6 was closed and then #5 was opened in order to let the sample expand into the two sampling loops. The pressure was read on MKS 1 for further calculations of our results. The stopcocks #7 and 8 and the two sampling loops were closed and the latter transferred to the gas chromatograph for analysis.

The shortest experiment that we were able to perform in this way lasted for 30 seconds.

Each mixture, stored in the mixing bulbs M_1 and M_2, was used for a series of experiments, performed at different reaction times or at different pressures. The reproducibility of our experimental technique was checked by repeating the same experiment with 2 or 3 identical mixtures prepared separately. A blank experiment

for each mixture (pyrolysis time = zero) was done to test for impurities. Our reported results are corrected for the presence of trace amounts of ethane and propylene in the starting mixtures.

Sampling technique

The sampling of the products of the reaction was done with 5 ml stainless steel loops (1/4" diameter) equipped at both ends with 1/8" Whitey ball valve and 1/8" tubing. Those loops were connected to the vacuum line, for sampling, and to Valco multiposition valves, for admission of the sample into the gas chromatograph, through 1/8" high vacuum Cajon fittings. The reproducibility of the system, as determined by injecting known amounts of a certified Matheson hydrocarbon mixture, was better than ±5%.

Analytical technique

The products resulting from the pyrolyses were analyzed by gas chromatography, with a flame ionization detector. Two analyses were made for each experiment, one using a Silicagel column to analyze ethane, another one using a Durapak (Phenylisocyanate/Porasil C) column to analyze propylene, 1-butene and 1,3-butadiene.

Silicagel column analysis

This column separated trace amounts of ethane from large amounts of methane and ethylene. The chromatographic conditions used were the following:

Column: 1.5m x 1/4" copper tubing, packed with 40-60 mesh silicagel

Carrier gas: N_2, 60 $ml.min^{-1}$

Temperature programming: 30°C for 8 min then +16°C.min^{-1} up to 250°C

A typical chromatogram of the analysis is shown on figure 3.

With our experimental conditions, the quantities of propylene and 1-butene were too small to detect quantitatively with this column.

Phenylisocyanate/Porasil C analysis

This column separated trace amounts of propylene from large amounts of ethylene. The chromatographic conditions used were the following:

Column: 6.0m x 1/4" aluminum tubing, packed with Durapak, phenylisocyanate on Porasil C 80-100 mesh

Carrier gas: N_2, 80 $ml.min^{-1}$

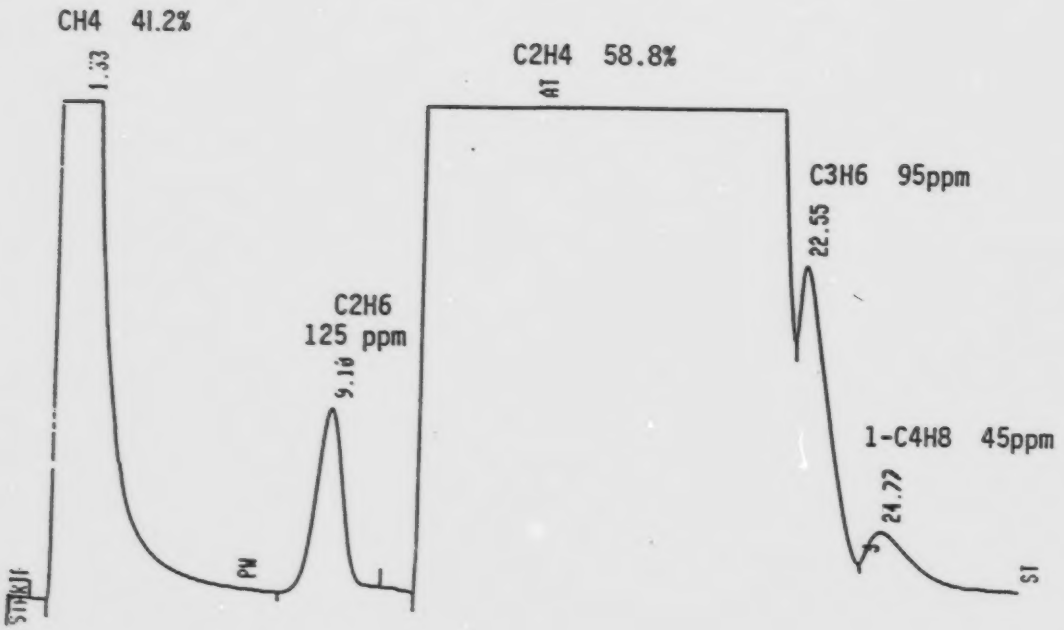
Temperature: isothermal at 25.5 ± 0.5°C

Retention times of C_2 to C_5 hydrocarbons obtained with those chromatographic conditions are the following:

- methane	3.20 min	- 1-butene	51 min
- ethane	4.50	- 1,3-butadiene	70
- ethylene	5.50	- isobutylene	71
- propane	8.00	- trans-2-butene	71
- acetylene	12.00	- cis-2-butene	77
- c-propane	15.00	- 1-pentene	130
- isobutane	16.40	- c-pentene	140
- propylene	18.40	- 2-pentenes	200
- n-butane	18.60	- 2-methyl-2-butene	210
- allene	22.40		

Both methods of analysis have been calibrated with a certified preset mixture obtained from Matheson Gas Products Canada. This mixture had the following composition:

- ethane	450 ± 9 ppm
- propylene	109 ± 2 ppm
- 1-butene	53.3 ± 1.1 ppm
- ethylene	balance



Column: Silicagel 40/60 mesh, 1.5m x 1/4"
Carrier gas: nitrogen, 60 ml/min
Sample: 5ml, 424Torr
Temperature: 30°C for 8 min, then +16°C/min up to 250

Figure 3

The Silicagel method was calibrated for ethane by measuring the peak area corresponding to a known amount of that compound. The phenylisocyanate/Porasil C method was calibrated for ethane, propylene and 1-butene, by measuring the peak height for ethane and the peak area for propylene and 1-butene. This method of analysis was not calibrated for 1,3-butadiene and a sensitivity equal to that of 1-butene was chosen arbitrarily for that compound.

RESULTS AND DISCUSSION

Summary

Fifty series of experiments have been done, 38 with ethylene-methane mixtures and 12 with 1-butene-ethylene-methane mixtures. A summary is given in table 1. Each series of experiments, with a certain composition of the mixture, consisted of between 3 and 13 runs at different times of pyrolysis. For each run, the amounts of ethane, propylene, 1-butene and 1,3-butadiene produced were determined. Reproducibility of the experimental procedure has been checked by repeating runs at a certain time of pyrolysis with mixtures of identical composition. A maximum scattering of ± 35% around an average value has been observed. For each series of experiments, an initial rate of formation was determined for ethane, propylene, 1-butene and 1,3-butadiene. Initial rates were calculated by extrapolating to zero time the rate of formation (quantity of product formed/time of pyrolysis), for each experiment, as a function of pyrolysis time. The error in the initial rates of formation of products was usually abount ± 30% but was as high as ± 50% in some cases where we had only 3 experimental points for the extrapolation.

Ethylene-Methane mixtures

Experiments with these mixtures have been done at three temperatures: 774, 824 and 853K. Results are reported in tables 2-a to 4-d.

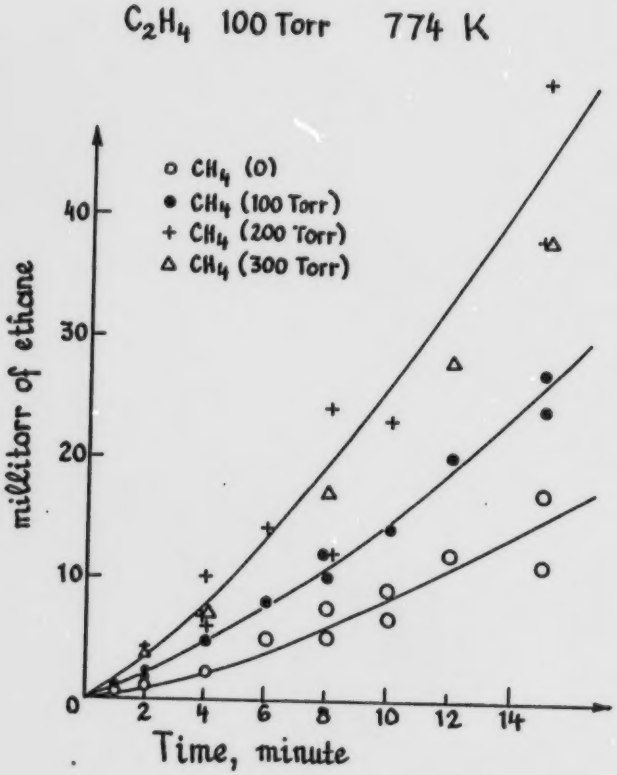
774K

The most extensive study was done at 774K. Experiments have been done with mixtures containing 14 to 200 Torr of ethylene and 0 to 400 Torr of methane. We have reported in the tables 2-a to 2-d the quantities of ethane, propylene, 1-butene and 1,3-butadiene produced as a function of pyrolysis time. The data are given as millitorr of product in the 0.21 liter reaction vessel at the temperature of the reaction. In table 7, we report the calculated initial rates of formation of those products. As an example we have plotted in figures 4 and 5 the quantities of ethane and propylene produced as a function of the time of pyrolysis, for the experiments done with 50 and 100 Torr of ethylene.

Propylene is always the major product. The reaction becomes self-accelarating at very low conversions, about 0.01%. We report in the following table, initial rates of formation of ethane, propylene, 1-butene and 1,3-butadiene obtained, from the pyrolysis of 100 and 200 Torr of pure ethylene, in this study and in a previous one done in the same temperature and pressure conditions by Back and Martin (1).

		Rate of product formation (10^{-12} mole.cm^{-3}.s^{-1})	
		Back & Martin	This study
C_2H_4 200 Torr	C_2H_6	0.53	0.5
	C_3H_6	3.64	6.1
	1-C_4H_8	0.62	1.2
	1,3-C_4H_6	0.23	0.4
C_2H_4 100 Torr	C_2H_6	0.17	0.2
	C_3H_6	0.63	0.9
	1-C_4H_8	0.24	0.3
	1,3-C_4H_6	0.08	0.2

This table shows a fairly good agreement between those two studies.


C_2H_4 100 Torr 774 K
o CH_4 (0)
• CH_4 (100 Torr)
+ CH_4 (200 Torr)
△ CH_4 (300 Torr)
millitorr of ethane
0
10
20
30
40
2
4
6
8
10
12
14
Time, minute

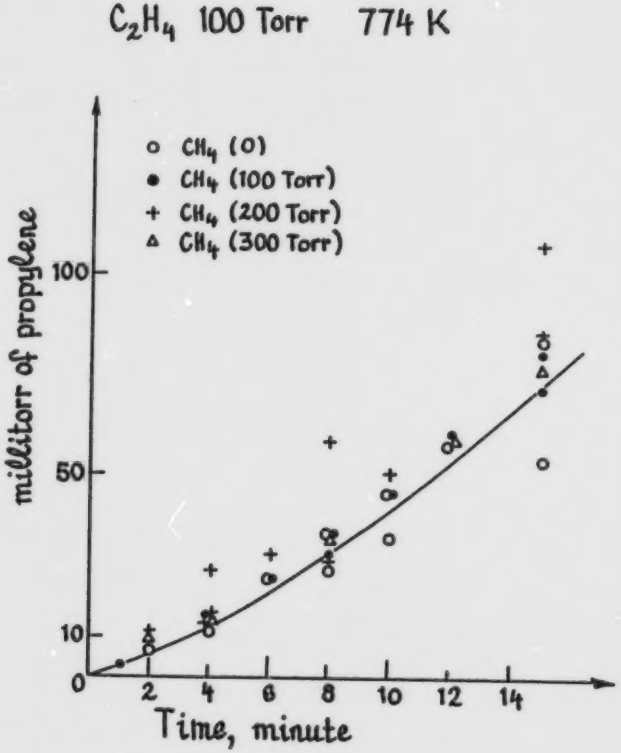
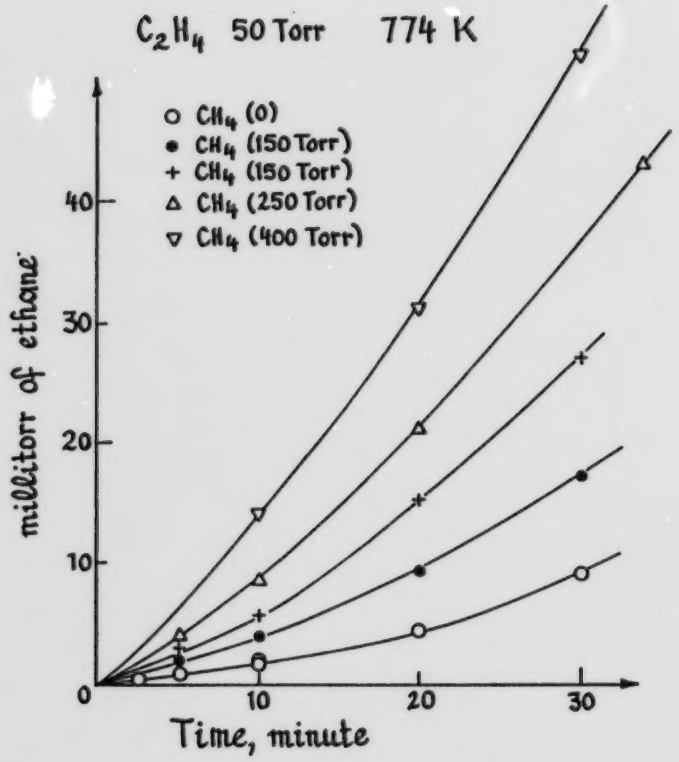

C_2H_4 100 Torr 774 K
o CH_4 (0)
• CH_4 (100 Torr)
+ CH_4 (200 Torr)
△ CH_4 (300 Torr)
millitorr of propylene
0
10
50
100
2
4
6
8
10
12
14
Time, minute

FIGURE 4


C_2H_4 50 Torr 774 K
○ CH_4 (0)
● CH_4 (150 Torr)
+ CH_4 (150 Torr)
△ CH_4 (250 Torr)
▽ CH_4 (400 Torr)
millitorr of ethane
0
10
20
30
40
Time, minute

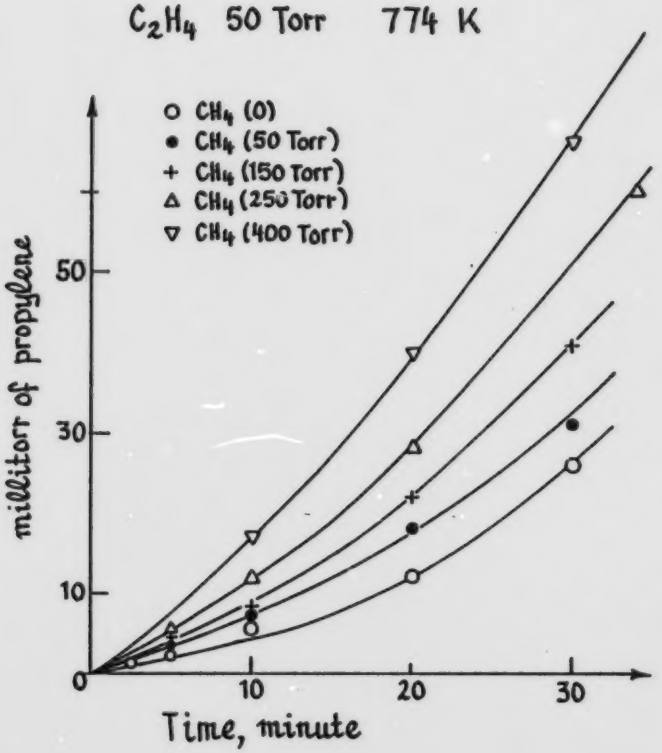

C_2H_4 50 Torr 774 K
○ CH_4 (0)
● CH_4 (50 Torr)
+ CH_4 (150 Torr)
△ CH_4 (250 Torr)
▽ CH_4 (400 Torr)
millitorr of propylene
0
10
30
50
Time, minute

FIGURE 5

Figure 6 shows a double logarithmic plot of the initial rate of formation of ethane, propylene and 1-butene as a function of the pressure of pure ethylene pyrolyzed. The order of the rate of formation of these products is respectively 2.0, 2.7 and 2.3, in good agreement with earlier results (1, 6, 7).

The addition of increasing quantities of methane to ethylene has the following effects:

1. it always substantially increases the quantity of ethane produced.
2. at 25 and 50 Torr of C_2H_4, it increases the quantity of propylene produced while at 100 and 200 Torr it has virtually no effect.
3. it has very little or no effect on the production of 1-butene and it has no effect on the production of 1,3-butadiene.

To examine the effect of the addition of CH_4 on the product distribution we have calculated the ratios of ethane, 1-butene and 1,3-butadiene to propylene. One main feature of the reaction is that the ratios $[C_2H_6]/[C_3H_6]$, $[C_4H_8]/[C_3H_6]$ and $[1,3\text{-}C_4H_6]/[C_3H_6]$ are constant for each type of mixture during the time of the pyrolysis. The results for ethane are plotted in figure 7. This figure shows that the addition of methane to ethylene always favors the production of ethane relatively to that of propylene. A limiting ratio of 0.8 seems to be reached at high methane pressure. The ratios $[1\text{-}C_4H_8]/[C_3H_6]$ and $[1,3\text{-}C_4H_6]/[C_3H_6]$ always drop with the addition of increasing quantities of methane.

We have plotted in figure 8 the relative rate of formation of ethane as a function of the initial ratio CH_4/C_2H_4 in the mixture. This clearly shows, especially for the experiments done with 25 and 50 Torr of ethylene that the formation of ethane is favored as methane is added to the system.

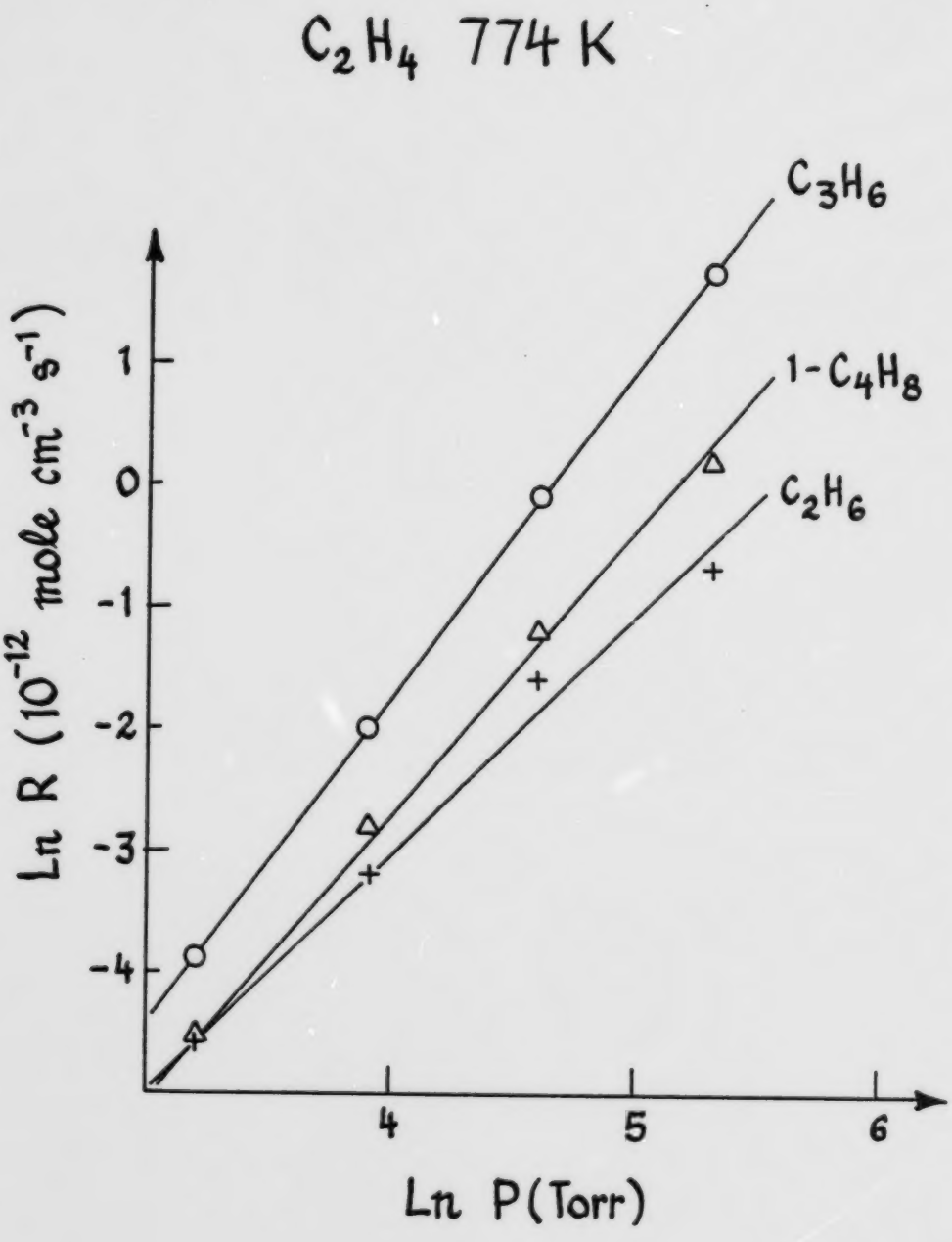

C_2H_4 774 K
C_3H_6
1-C_4H_8
C_2H_6
Ln R (10^{-12} mole cm^{-3} s^{-1})
1
0
-1
-2
-3
-4
4
5
6
Ln P(Torr)

FIGURE 6

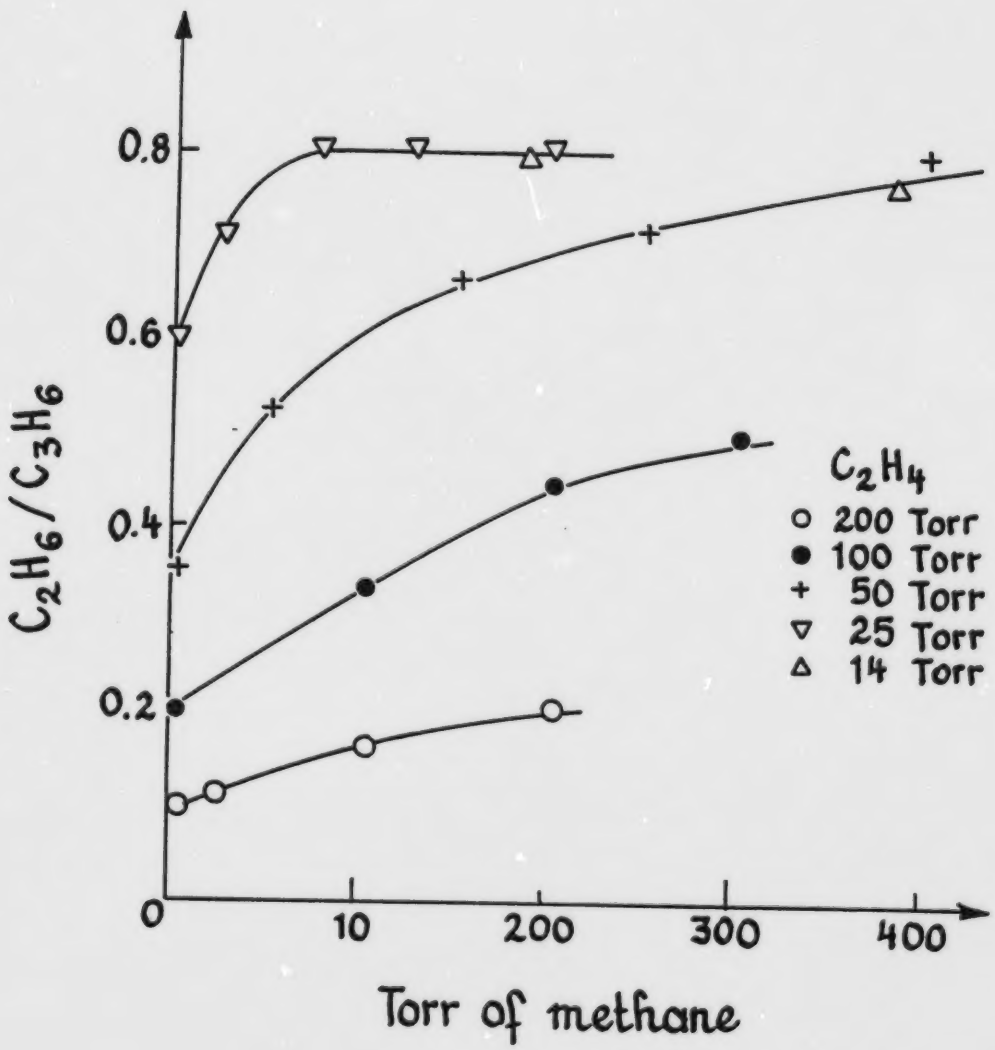

C_2H_4 774 K
0.8
0.6
0.4
0.2
0
C_2H_6/C_3H_6
10
200
300
400
Torr of methane
C_2H_4
200 Torr
100 Torr
50 Torr
25 Torr
14 Torr

FIGURE 7

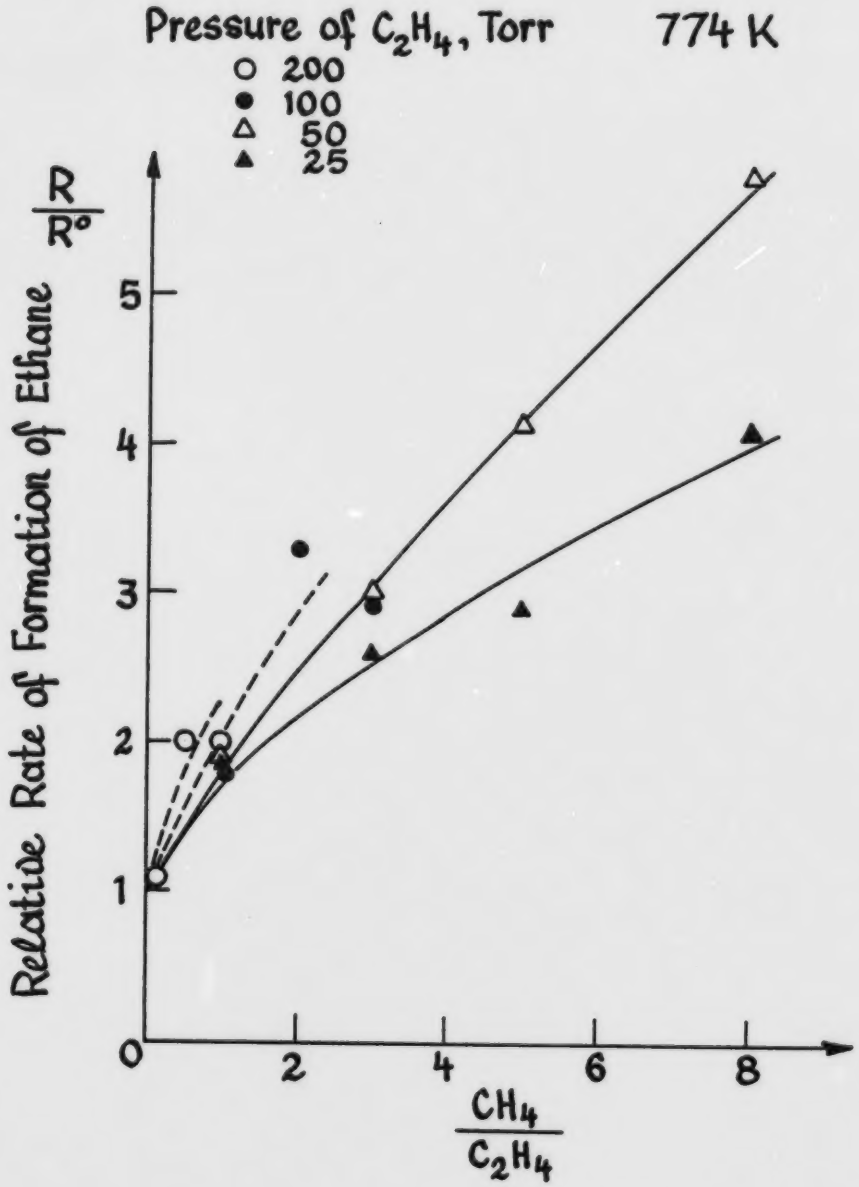

Pressure of C_2H_4, Torr
774 K
200
100
50
25
Relative Rate of Formation of Ethane $\frac{R}{R^\circ}$
0
1
2
3
4
5
2
4
6
8
$\frac{CH_4}{C_2H_4}$

FIGURE 8

824K

Three series of experiments have been done at 824K with 50, 25 and 12.5 Torr of ethylene and 0 to 350 Torr of methane. We have reported in tables 3-a to 3-d the quantities of ethane, propylene, 1-butene and 1,3-butadiene produced as a function of pyrolysis time. In table 8 we report the initial rates of formation of those products.

At long pyrolysis time, propylene is always the major product. In the initial stage of the pyrolysis of pure ethylene, ethane, 1-butene or 1,3-butadiene may be produced in larger quantities. When methane is added to ethylene, propylene is always the major product, at long pyrolysis time as well as in the initial stage of the reaction. The ratios of ethane, 1-butene and 1,3-butadiene to propylene all decrease as the reaction proceeds, in the presence or in the absence of methane. The ratio ethane/propylene, calculated at zero-time, is constant (50 Torr ethylene) or decreases (25 and 12.5 Torr ethylene) when increasing amount of methane are added to ethylene. The ratios 1-butene/propylene and 1,3-butadiene/propylene always decrease in the same conditions. The production of propylene relative to that of the other major products is favored at that temperature, when methane is added as a reactant.

The addition of increasing quantities of methane in the initial mixture has the following effects on the absolute quantities of products:

1. the quantities of ethane and propylene produced are always increased
2. the quantity of 1-butene produced is always decreased
3. the quantity of 1,3-butadiene produced is unaffected.

At 50, 25 and 12.5 Torr of ethylene, the initial rate of formation of propylene is increased more than that of ethane.

853K

Three series of experiments have been done at 853K with 50, 25 and 12.5 Torr of ethylene and 0 to 350 Torr of methane. We have reported in tables 4-a to 4-d the quantities of ethane, propylene, 1-butene and 1,3 butadiene produced as a function of pyrolysis time. In table 9, we report the initial rate of formation of those products. The behavior of those mixtures at 853K is very similar to that at 824K. The ratios ethane/propylene, 1-butene/propylene and 1,3-butadiene/propylene all decrease when the reaction proceeds. The initial value (at zero-time) of those ratios also decreases when increasing quantities of methane are added to ethylene in the initial mixture, indicating clearly that the production of propylene is favored relative to that of the other products. As observed at 824K, the addition of methane to ethylene increases the rate of production of ethane and propylene, decreases the rate of production of 1-butene and has no effect on the production of 1,3-butadiene. At 50, 25 and 12.5 Torr of ethylene, the initial rate of formation of propylene is increased morethan that of ethane, this effect being even more important than that observed at 824K.

Discussion

A reaction pathway representing the chemistry of the thermal reaction of ethylene-methane mixtures must account for the following experimental results:

1. the addition of methane to ethylene always increases the rate of formation of ethane and propylene while the rate of formation of 1-butene usually decreases or stays the same.

2. at the lowest temperature studied, 774K, the addition of increasing amount of methane to ethylene favors the production of ethane relative to that of propylene while at higher temperature the opposite is observed. This is illustrated in figure 9

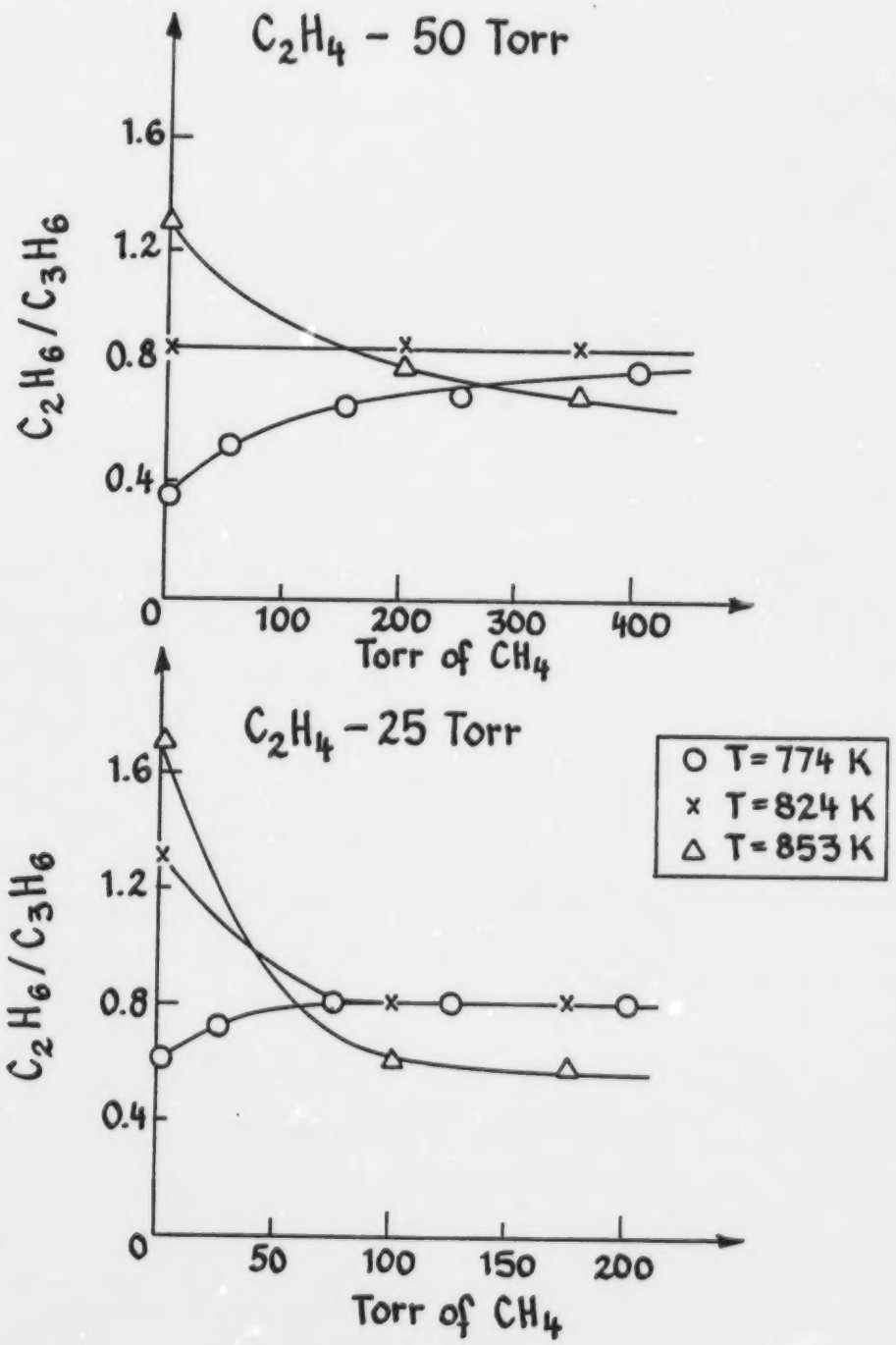

C_2H_4 - 50 Torr
C_2H_6/C_3H_6
1.6
1.2
0.8
0.4
0
100
200
300
400
Torr of CH_4
C_2H_4 - 25 Torr
C_2H_6/C_3H_6
1.6
1.2
0.8
0.4
0
50
100
150
200
Torr of CH_4
○ T = 774 K
× T = 824 K
△ T = 853 K

FIGURE 9

in which we have plotted the ratio $[C_2H_6]/[C_3H_6]$ as a function of the amount of methane in the initial mixture, calculated for 50 and 25 Torr of ethylene at the three temperatures studied.

3. the addition of increasing quantities of methane to ethylene always favors the production of propylene relative to that of 1-butene or 1,3-butadiene, the effect becoming more important as the temperature increases.

Previous studies (1, 2, 6, 7) of the thermal reaction of ethylene around 500°C have concluded that the initiation step in the chain reaction mechanisms the disproportionation of ethylene:

[1] $C_2H_4 + C_2H_4 \text{ ----> } C_2H_3 + C_2H_5$

The two radicals so created will further react with ethylene and initiate two parallel and interacting series of reactions, as reported thereafter:

[3] $C_2H_5 + C_2H_4 \text{ ----> } C_2H_6 + C_2H_3$

[6] $C_2H_5 + C_2H_4 \text{ ----> } C_4H_9$

[7] $C_4H_9 + C_2H_4 \text{ ----> } n\text{-}C_6H_{13}$

[8] $n\text{-}C_6H_{13} \text{ -----> } 2\text{-}C_6H_{13}$

[9] $2\text{-}C_6H_{13} \text{ -----> } C_3H_6 + n\text{-}C_3H_7$

[10] $n\text{-}C_3H_7 + C_2H_4 \text{ ----> } 1\text{-}C_5H_{11}$

[11] $1\text{-}C_5H_{11} \text{ -----> } 2\text{-}C_5H_{11}$

[12] $2\text{-}C_5H_{11} \text{ ----> } C_3H_6 + C_2H_5$

[13] $n\text{-}C_6H_{13} \text{ -----> } 3\text{-}C_6H_{13}$

[14] $3\text{-}C_6H_{13} \text{ -----> } 1\text{-}C_4H_8 + C_2H_5$

[15] $3\text{-}C_6H_{13} \text{ -----> } 1\text{-}C_5H_{10} + CH_3$

[16] $CH_3 + C_2H_4 \text{ ----> } CH_4 + C_2H_3$

[17] $CH_3 + C_2H_4 \text{ ----> } n\text{-}C_3H_7$

[18] $C_2H_3 + C_2H_4 \text{ ----> } C_4H_7$

[19] $C_4H_7 + C_2H_4 \text{ ----> } C_6H_{11}$

[20] $C_6H_{11} \text{ ----> } C_4H_6 + C_2H_5$

At 853K and below, the rate of thermal dissociation of methane is negligible and consequently the formation of methyl radicals and hydrogen atoms through that route is of no importance.

In this mechanism only the two products, methane and ethane are formed by an abstraction reaction from ethylene, reactions [16] and [3] respectively. Other products, such as propylene or 1-butene, are formed following addition to ethylene, isomerization and decomposition. Addition of a saturated hydrocarbon, such as methane, offers an alternative source of abstractable hydrogen for the methyl and ethyl radicals, but clearly does not offer a new route for addition reactions. Thus the addition of methane should lead to an increase in the rate of formation of ethane, through the new abstraction reaction,

[21] $C_2H_5 + CH_4 \text{ ----> } C_2H_6 + CH_3$

The increase in the rate of formation of ethane in the presence of methane is therefore reasonably accounted for by the mechanism.

Other radicals present in the system may also undergo reactions similar to [21]. For radicals of carbon number ≥3 this reaction is probably too endothermic and therefore too slow to compete with addition to ethylene. Saturated hydrocarbons of carbon number ≥3 were not important products. The only radicals for which abstraction may be sufficiently fast are probably methyl (where reaction is not observable), ethyl and vinyl. In pure ethylene hydrogen abstraction by vinyl radicals is not observable, but probably occurs, just as the abstraction by ethyl radicals occurs, as shown by the formation of the product ethane. In the presence of

methane, abstraction from methane may also occur.

[22] $$C_2H_3 + CH_4 \text{ ----> } C_2H_4 + CH_3$$

Reaction [22] is not directly observable in our system but its occurence may be deduced by the effect of the exchange of vinyl radicals for methyl radicals. The chain-propagating reactions of both ethyl and methyl radicals lead to the formation of propylene but butene is formed only by reactions of the ethyl and vinyl radicals. A shift in the relative concentration of the methyl and vinyl radicals could lead to an increase in the yield of propylene and possibly a decrease in the yield of butene .

The fact that the increase in rate of formation of ethane is more pronounced at lower temperature while that of propylene is more important at higher temperature is not so readily apparent. The two reactions [21] and [22] should have similar rate constants and activation energies so that relative importance should not change greatly over the temperature range of these experiments. The further reactions of the methyl radical which lead to propylene involve decomposition reactions of radicals and such reactions have temperature coefficients larger than those of abstraction reactions such as [21] and [22]. Thus formation of propylene may be favored at high temperature due to reactions such as [9] and [12].

It is worth pointing out some particular features of the present system involving the thermal reactions of ethylene at temperatures in the neighbourhood of 500°C. First, it is clear from the results that methane is converted directly to the two products, ethane and propylene. Ethylene therefore acts as a sensitizer for the decomposition of methane and has several advantages in this role. Radicals are initiated in ethylene at fairly low temperatures and because of the high reactivity of ethylene towards radicals a chain decomposition and polymerization occurs with a long chain length. The activation energy for the reaction is about 48 $kcal.mol^{-1}$,

much lower than the corresponding activation energy for decomposition of saturated hydrocarbons. Thus ethylene is effective at temperatures lower than those required using a saturated hydrocarbon as sensitizer. The main chain-propogating radicals are ethyl, methyl and vinyl, which give ethane and propylene directly, as well as other products. The relative yields of ethane and propylene were related to the relative concentrations of ethyl and methyl radicals in the system. This ratio was a function of temperature and relative amount of methane so that the relative importance of the two products, ethane and propylene, could be altered by the choice of conditions. Finally, an obvious advantage is that only hydrocarbon products are formed.

1-Butene-Ethylene-Methane mixtures

Experiments with these mixtures in various proportions have been done at 774 and 853K.

774K

Experiments have been done at this temperature with mixtures containing 25 or 50 Torr of ethylene and 0 to 400 Torr of methane, with 1-butene representing around 4% of ethylene. Experiments with pure 1-butene and 1-butene-methane mixtures have also been done. These results, as well as the results of corresponding pure ethylene experiments are reported in tables 5-a to 5-d. As an example we have reported in figure 10 the quantities of ethane obtained as a function of pyrolysis time for the different series of experiments done. In table 10, we report the calculated initial rates of formation of ethane, propylene and 1,3-butadiene.

The main product of the pyrolysis of pure 1-butene is propylene. The other major products detected are in order of importance, methane, ethylene, 1,3-butadiene and ethane. Smaller quantities of cis,2-butene, cyclopentene and 1-pentene are also produced. Trans,2-butene is also probably produced but could not be analyzed with the present columns. The addition of large quantities of methane to 1-butene has very little or no effect on the production of ethane, propylene or 1,3-butadiene.

The main product of the pyrolysis of 1-butene-ethylene mixtures is also propylene. Ethane and 1,3-butadiene are next in importance and pentenes (cyclopentene + 1-pentene) are produced in quantities of the same order as those of 1,3-butadiene. Cis,2-butene is also produced and represents 3 to 8% of 1,3-butadiene. The addition of large quantities of methane to 1-butene-ethylene mixtures

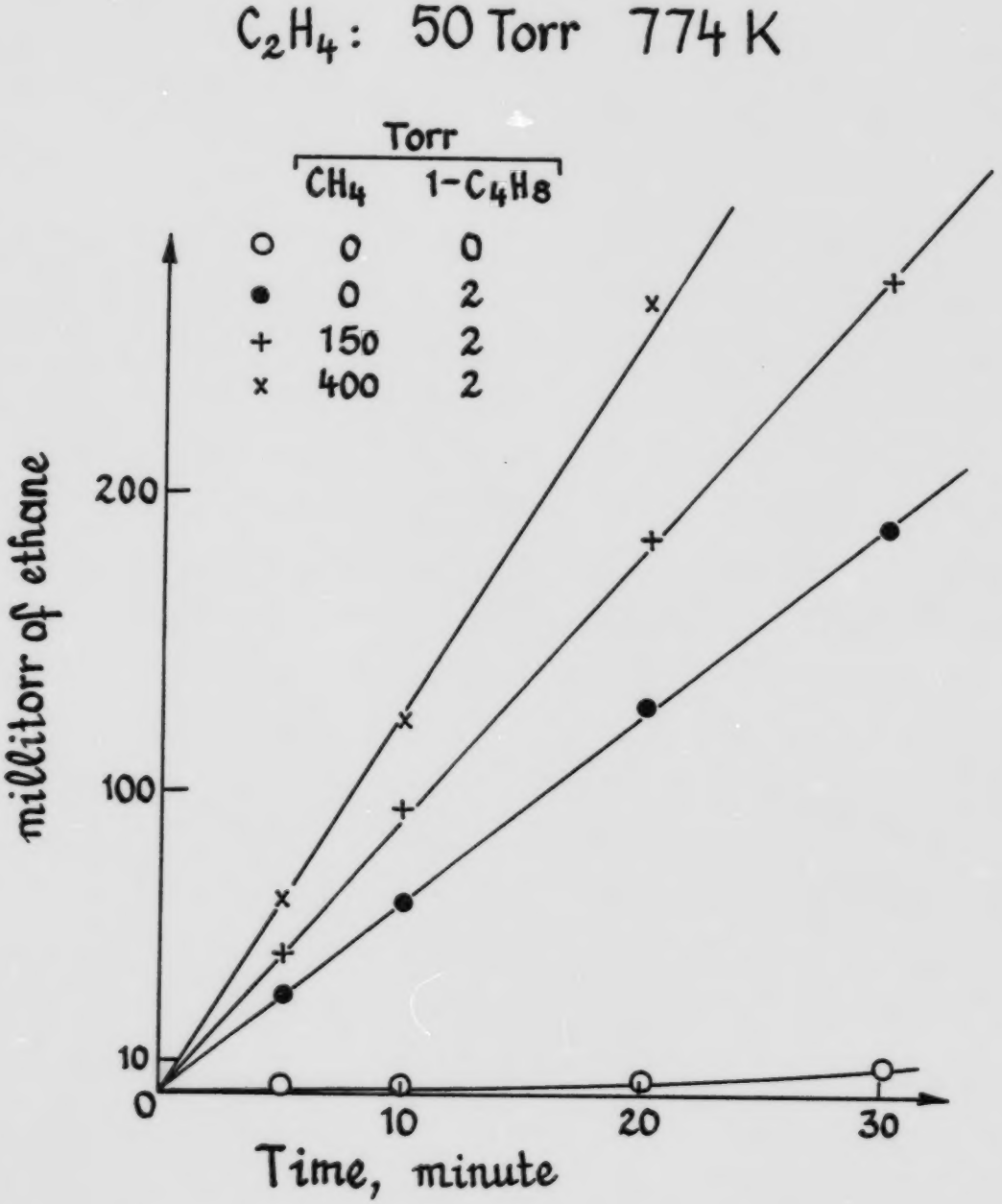

C_2H_4: 50 Torr 774 K
Torr
CH_4 $1\text{-}C_4H_8$
○ 0 0
● 0 2
+ 150 2
× 400 2
millitorr of ethane
200
100
10
0
10
20
30
Time, minute

FIGURE 10

has no effect on the production of propylene and 1,3-butadiene but significantly increases the production of ethane.

The main observation about 1-butene is that its concentration decreases linearly with time (in the time range of our experiments) and that its rate of consumption is nearly the same regardless of the presence of methane or ethylene in the initial mixture. In spite of this constant consumption of 1-butene, in the presence or absence of ethylene as a starting reactant, much larger quantities of ethane, propylene and 1,3-butadiene are produced when 1-butene and ethylene are pyrolyzed simultaneously. For ethane, the initial rates of formation are respectively roughly 50 and 15 times more important than in the case of pure ethylene and pure 1-butene. The effect is less important for propylene and even less important for 1,3-butadiene. The addition of large amounts of methane to 1-butene-ethylene mixtures has no effect on the rates of formation of propylene and 1,3-butadiene while the rate of formation of ethane is significantly increased.

853K

Experiments have been done with mixtures containing 25 and 50 Torr of ethylene, 1-butene (4% of ethylene) and 0 or 400 Torr of methane. These results, as well as the results of the corresponding pure ethylene experiments, are reported in tables 6-a to 6-d. Again as an exemple we report in figure 11, the quantities of ethane produced as a function of pyrolysis time for the different series of experiments done at that temperature. In table 11, we report the calculated initial rates of formation of ethane, propylene and 1,3-butadiene.

Results are very similar to those observed at 774K. The main products are in order of importance, propylene, methane, 1,3-butadiene and ethane. Butenes and pentenes are also produced but in smaller quantities.

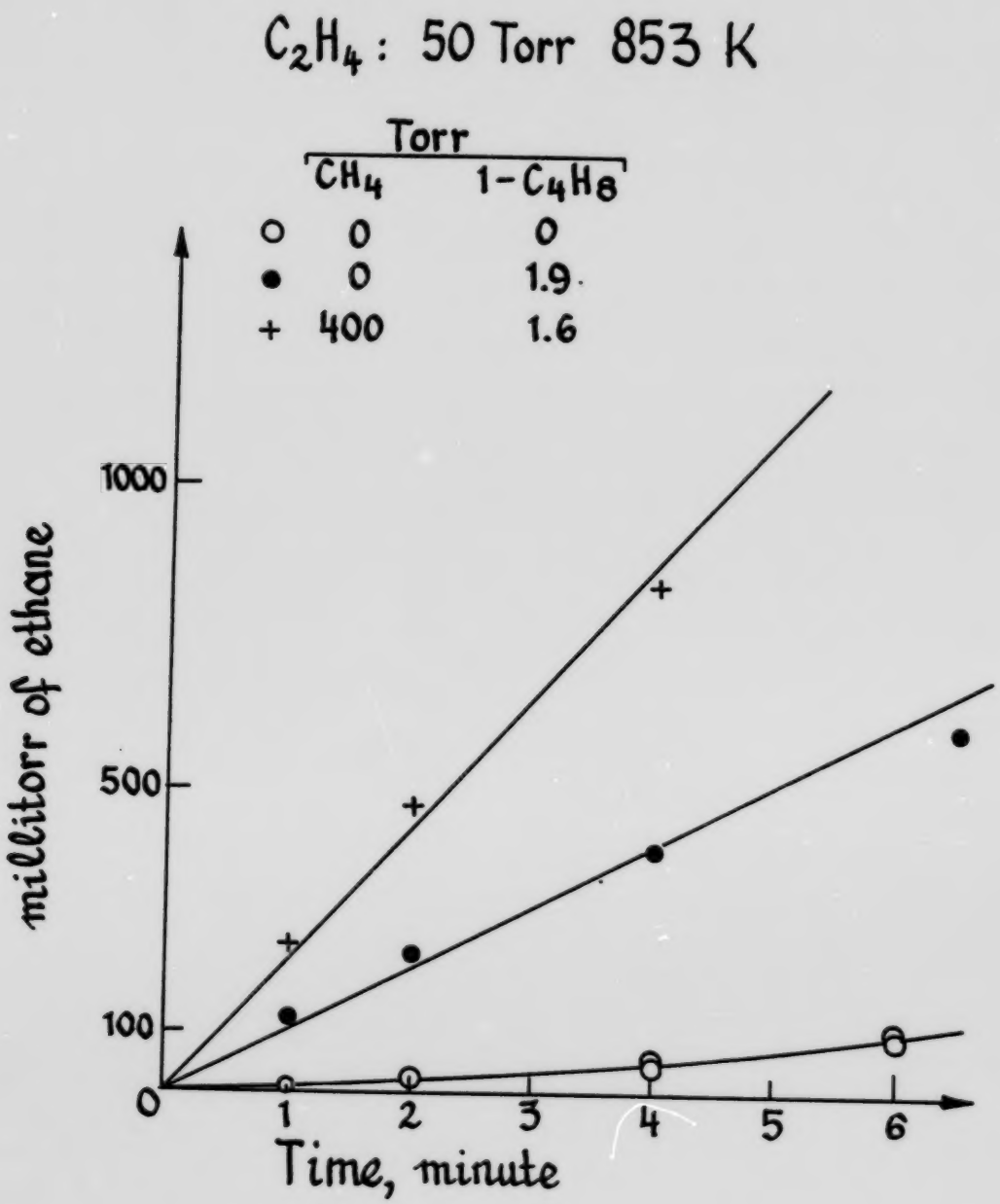

C_2H_4 : 50 Torr 853 K
Torr
CH_4 $1-C_4H_8$
○ 0 0
● 0 1.9
+ 400 1.6
millitorr of ethane
1000
500
100
0
1
2
3
4
5
6
Time, minute

FIGURE 11

Table 11 clearly shows that the addition of 4% 1-butene to ethylene drastically increases the rate of formation of all products, by a factor 40 for ethane, a factor 200 for propylene and a factor 100 for 1,3-butadiene. As in the case of the experiments done at 774K, the consumption of 1-butene is the same in the presence or absence of methane. The rates of formation of propylene and 1,3-butadiene stay unchanged or are slightly reduced when methane is added to the initial mixture while the rate of formation of ethane is significantly increased in the same conditions.

Discussion

The two main features of these experiments are:

1. the simultaneous pyrolysis of 1-butene and ethylene produces much larger quantities of ethane, propylene and 1,3-butadiene than the pyrolysis of pure 1-butene or of pure ethylene.
2. the addition of methane to 1-butene-ethylene mixtures has no effect on the consumption of 1-butene and on the production of propylene and 1,3-butadiene while it significantly increases the production of ethane.

Previous studies of the kinetics of the pyrolysis of ethylene in the presence of 1-butene had shown that the increase in the rate of formation of all products was a result of the thermal dissociation of 1-butene:

[23] $$1\text{-}C_4H_8 \text{ -----> } C_3H_5 + CH_3$$

which had the effect of increasing the rate of initiation of radicals in the system. The importance of this dissociation is clearly seen by the marked decrease in concentration of 1-butene during the course of the reaction, even though it is being formed as a product of the reaction. The methyl and allyl radicals enter into chain

propagating steps, similar to those outlined earlier, and are soon converted to ethyl and vinyl radicals in the presence of the large excess of ethylene. Thus the rates of formation of all the major products for the pyrolysis of ethylene itself are increased in the presence of 1-butene.

Addition of methane to the mixtures of 1-butene and ethylene caused a significant increase in the rate of formation of ethane. In these mixtures, three abstraction reactions of ethyl radicals are possible.

[3] $C_2H_5 + C_2H_4 \text{----> } C_2H_6 + C_2H_3$

[21] $C_2H_5 + CH_4 \text{-----> } C_2H_6 + CH_3$

[24] $C_2H_5 + 1\text{-}C_4H_8 \text{----> } C_2H_6 + C_4H_7$

all leading to ethane.

On the other hand, addition of methane appeared to have little effect on the rate of formation of propylene. The corresponding abstraction reactions of the vinyl radical (which led to formation of propylene on mixtures of ethylene and methane) are as follows:

[22] $C_2H_3 + CH_4 \text{----> } C_2H_4 + CH_3$

[25] $C_2H_3 + 1\text{-}C_4H_8 \text{----> } C_2H_4 + C_4H_7$

k_{25} is much larger than k_{22} and in the presence of even a small quantity of 1-butene may compete successfully with reaction [22]. Abstraction from 1-butene does not, however, lead to formation of a methyl radical and hence to propylene. The C_4 radical formed in [25] very likely leads to formation of higher molecular weight products.

The absence of effect of the addition of methane on the rate of formation of propylene also shows that the allyl radicals, formed through the decomposition reaction of 1-butene [23], are not reacting with methane by abstracting an hydrogen atom to form propylene. The only reactions of allyl radicals are their

addition to ethylene or 1-butene to form higher molecular weight products.

To summarize, addition of 1-butene to the mixtures of ethylene and methane had two main effects. First, 1-butene provided an increase in the rate of initiation and hence an increase in the rate of production of radicals in the system. In a sense, 1-butene acts as a sensitizer for the ethylene reactions, with the result that the same rate of formation of products may be acheived at a lower temperature. Secondly, 1-butene changes the product distribution, even with the relatively small amounts added. With 1-butene present, methane enhanced the rate of formation of ethane but did not appreciably alter the rate of formation of propylene. Such an additive may be useful in providing a particular selectivity.

CONCLUSION AND RECOMMENDATIONS

The results of the present study have shown that homogeneous, thermal gas phase radical reactions can lead to significant conversion of methane to higher hydrocarbons. As well, the selectivity of the products, particularly the yields of ethane and propylene, may be altered by choice of reaction conditions or additive.

We recommend the continuation of the study of homogeneous thermal reactions as a practical route to conversion of methane. In particular, studies of these systems at higher conversions and over wider temperature ranges, should provide much useful data. This could be realized by two different approaches:

1. by studying more extensively the influence of the addition of 1-butene and of other additives such as neopentane, isobutane or hexamethylethane. This would allow studies of the conversion of methane with lower pressures of ethylene and at lower temperatures, where the production of ethane is favored relatively to that of propylene, while maintaining reasonably high rates of formation of the products.

2. by studying the pyrolysis of ethylene-methane mixtures at higher temperatures. This would allow a higher conversion of the reactants and so may provide a direct evidence of the incorporation of methane into higher hydrocarbons. Much larger rates of formation of products are expected as the temperature is increased, particularly those of ethane and propylene.

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Ethylene, methane and 1-butene content (in Torr) of the mixtures pyrolyzed at 774K, 824K and 853K.

		774K	824K	853K
Ethylene			Methane	
200		0, 20, 100, 200		
100		0, 100, 200, 300		
50		0, 50, 150, 250, 400	0, 200, 350	0, 200, 350
25		0, 25, 75, 125, 200	0, 100, 175	0, 100, 175
14		186, 286		
12.5			0, 50, 87.5	0, 50, 87.5
Ethylene	1-butene			
0	1, 2	0		
50	2	0, 150, 400		0, 400
25	1	0, 75, 200		0, 200

Table-1

Quantities of C_2H_6 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 774K

C_2H_4	CH_4	Time 30	45	60	90	120	180	240	300	360
200	0	0.8	1.3		2.5	3.3	5.8	8.6	11	12
						3.2	6.2	8.4	11	13
200	20			1.7	2.9	3.8	6.2	9.3	13	17
										17
200	100			3.5		6.8		17		29
				2.8		6.8				
200	200			3.7		7.1	11	17	22	32
				3.0			11			28
										25

		Time 60	120	240	360	480	600	720	900
100	0	0.7	0.9	2.2	4.9	7.5	9.0	12	17
						5.2	6.6		11
100	100	1.0	2.4	4.8	7.9	12	14	20	27
			1.9			10			24
100	200		4.2	10	14	24	23		51
				5.8		12			38
				6.8					
100	300		4.0	7.0		17		28	38

		Time 150	300	600	1200	1800	2040
50	0	0.5	0.8	1.7	4.3	8.9	
				1.9			
50	50		1.9	3.9	9.2	17	
50	150		2.8	5.5	15	27	
50	250		4.0	8.4	21		43
50	400			14	31	52	

		Time 300	600	1200	2400	2520	2640	3600
25	0	0.3	0.6	1.1		3.4		6.8
			0.5					
25	25		1.0	2.7	5.6			12
25	75		1.7	3.6	9.9			18
25	125		2.5	4.5			15	20
25	200			7.1	17			28

		Time	1800	3600	7200
14	186		5.1	14	29
			4.7		
14	386		8.5	14	36

Table 2-a

Quantities of C_3H_6 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 774K

C_2H_4	CH_4	Time 30	45	60	90	120	180	240	300	360
200	0	9.5	14		28	36	58	86	102	120
						33	63	78	107	123
200	20			15	27	34	53	83	109	142
										142
200	100			21		44		110		180
				18		44				
200	200			18		36	56	88	115	161
				14			54			145
										126

		Time 60	120	240	360	480	600	720	900
100	0		5.9	11	24	35	45	57	83
						26	34		53
100	100	2.7	7.1	15	24	35	45	60	80
			5.2			30			71
100	200		11	26	30	58	50		107
				13		28			85
				15					
100	300		8.1	14		34		58	76

		Time 150	300	600	1200	1800	2040
50	0	1.4	2.3	5.4	12	26	
				5.3			
50	50		3.7	7.3	18	31	
50	150		4.3	8.3	22	41	
50	250		5.6	12	28		60
50	400			17	40	66	

		Time 300	600	1200	2400	2520	2640	3600
25	0	0.4	0.9	2.0		6.1		12
			0.9					
25	25		1.3	3.9	7.7			18
25	75		2.1	4.5	12			22
25	125		3.1	5.5			19	25
25	200			8.8	22			35

		Time	1800	3600	7200
14	186		6.4	18	36
			6.3		
14	386		12	19	48

Table 2-b

Quantities of 1-C_4H_8 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 774K

C_2H_4	CH_4	Time	30	45	60	90	120	180	240	300	360
200	0		2.0	2.5		5.4	7.3	13	17	24	22
							6.7	13	16	22	26
200	20				3.2	5.2	6.8	11	16	22	29
											28
200	100				4.1		7.9		20		33
					3.4		8.2				
200	200				3.3		6.1	10	16	19	30
					2.4			10			28
											22

		Time	60	120	240	360	480	600	720	900
100	0			2.0	3.6	7.3	11	13	17	24
							7.6	10		16
100	100		0.6	1.1	3.4	5.3	8.5	10	14	18
							6.6			14
100	200			1.9	5.0	6.2	11	10		20
					2.4		5.8			16
					3.7					
100	300			1.3	2.3		5.7		10	13

		Time	300	600	1200	1800	2040
50	0		1.1	2.3	5.4	12	
				2.5			
50	50		0.9	2.1	5.2	8.9	
50	150		0.7	1.4	4.1	7.6	
50	250		0.5	1.4	3.8		7.9
50	400			1.5	3.8	6.4	

		Time	600	1200	2400	2520	2640	3600
25	0		0.6	1.3		3.9		7.6
			0.5					
25	25		0.4	1.4	2.8			6.3
25	75		0.5	0.8	2.4			4.2
25	125		0.4	0.7			2.4	3.3
25	200			0.7	1.8			3.1

		Time	1800	3600	7200
14	186		0.3	0.9	1.8
			0.3		
14	386		0.3	0.5	1.3

Table 2-c

Quantities of 1,3-C_4H_6 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 774K

C_2H_4	CH_4	Time 30	45	60	90	120	180	240	300	360
200	0	0.6	1.2		1.9	2.6	4.1	5.8	7.3	8.3
						2.9	4.6	5.7	7.7	8.1
200	20			0.9	2.0	2.4	3.8	5.5	7.5	9.0
										9.4
200	100			1.3		2.7		7.2		11
				1.2		2.8				
200	200			1.0		2.2	3.4	5.3	6.7	9.0
								3.2		7.7

		Time	120	240	360	480	600	720	900
100	0		1.0	1.9	3.6	4.9	6.7	7.9	11
						3.9	4.3		6.9
100	100		0.9	1.7	2.7	3.8	4.9	6.4	8.3
						3.4			7.2
100	200		1.1	2.6	3.7	5.9	5.0		9.9
				1.3		2.8			8.4
				1.5					
100	300		1.0	1.7		3.2		5.0	6.7

		Time	300	600	1200	1800	2040
50	0		0.7	1.1	3.2	6.2	
				1.7			
50	50				3.4	5.9	
50	150			1.3	2.9	6.6	
50	250		0.7	1.5	3.9		7.4
50	400			1.9	4.4	7.0	

		Time	1200	2400	2520	2640	3600
25	0		0.9		2.6		5.0
25	25		0.9	2.1			5.0
25	75			2.8			4.4
25	125		1.1			3.4	4.5
25	200			4.3			5.5

		Time	1800	3600	7200
14	186		1.1	3.1	5.8
			0.9		
14	386		1.3	2.3	5.6

Table 2-d

Quantities of C_2H_6 formed (in millitorr in a 210 cm^3 reactor),
as a function of pyrolysis time (second).
T = 824K

C_2H_4	CH_4	Time 60	120	240	360	480	600	720	900
50	0	1.0	2.3 2.8	6.1	12		31	44	65
50	200		5.7	18		48			122
50	350		9.5	23		61			159

		Time 120	240	480	720	1080	1200
25	0	0.6	1.5	4.2 4.1	7.8	17	22
25	100		4.9	12	23		48
25	175		6.6	17	29		77

		Time 120	300	600	1200	1800	2400	3600
12.5	0	0.1	0.2	0.7	2.6 3.2	5.2	12	21
12.5	50			3.7	10		30	59
12.5	87.5			5.6	15		43	74

Table 3-a

Quantities of C_3H_6 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 824K

C_2H_4	CH_4	Time 60	120	240	360	480	600	720	900
50	0	1.1	2.7 3.4	7.5	15		41	57	87
50	200		6.7	21		54			138
50	350		12	27		71			177

		Time 120	240	480	720	1080	1200
25	0	0.5	1.3	3.9 3.8	7.5	18	24
25	100		6.4	16	28		60
25	175		8.3	21	37		96

		Time 120	300	600	1200	1800	2400	3600
12.5	0	0.1	0.2	0.6	2.3 2.8	4.9	12	25
12.5	50			5.6	15		44	85
12.5	87.5			9.2	24		68	112

Table 3-b

Quantities of 1-C_4H_8 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 824K

C_2H_4	CH_4	Time 60	120	240	360	480	600	720	900
50	0	0.9	2.3 2.8	6.3	12		29	38	53
50	200		0.8	3.0		7.6			19
50	350		1.1	2.4		6.2			16

		Time	240	480	720	1080	1200
25	0		1.4	4.1 3.7	7.3	14	17
25	100		0.8	1.9	3.6		7.0
25	175		0.6	1.6	2.9		7.4

		Time	300	600	1200	1800	2400	3600
12.5	0		0.2	0.6	2.0 2.5	3.7	7.4	10
12.5	50			0.5	1.3		3.5	6.0
12.5	87.5			0.4	1.3		3.3	5.0

Table 3-c

Quantities of 1,3-C_4H_6 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 824K

C_2H_4	CH_4	Time 60	120	240	360	480	600	720	900
50	0	0.8	2.4 2.9	6.4	12		28	38	54
50	200		2.1	6.8		16			40
50	350		3.0	7.0		18			42

		Time	240	480	720	1080	1200
25	0		1.5	4.9 4.9	9.3	19	24
25	100		2.6	6.1	11		23
25	175		2.7	6.6	11		30

		Time	300	600	1200	1800	2400	3600
12.5	0		0.5	1.2	4.0 4.2	7.5	16	26
12.5	50			2.5	6.9		19	34
12.5	87.5			3.2	8.6		23	36

Table 3-d

Quantities of C_2H_6 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 853K

C_2H_4	CH_4	Time 30	60	120	240	360
50	0	2.0	5.7	19	45	88
			5.3		56	107
			5.5			
50	200	3.3	10	28	90	170
			9.5			
50	350	4.9	11	31	95	172
			9.5			

	Time	60	120	240	360	600	900
25	0	1.1	3.1	18	20	44	100
		1.8	5.7	16	30		80
							96
25	100	2.6	9.2	24	49	100	169
25	175	3.4	7.9	30	44	89	165
			8.5	24			
			7.3				

	Time	120	240	480	720	1200	1800
12.5	0	1.6	4.5	13	20	38	54
		1.6				35	
12.5	50	2.5	10	19	30	57	89
			6.9				
12.5	87.5	1.8	6.1	14	24	48	112
			4.9		24		83
			4.6				

Table 4-a

Quantities of C_3H_6 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 853K

C_2H_4	CH_4	Time 30	60	120	240	360
50	0	1.6	4.5	17	44	94
			4.4		54	122
			4.3			
50	200	4.6	13	35	105	202
			12			
50	350	6.8	15	41	120	217
			13			

	Time	60	120	240	360	600	900
25	0	0.8	2.2	16	17	47	95
		1.2	4.0	14	28		124
							127
25	100	4.2	14	34	68	138	228
25	175	5.7	13	49	69	138	248
			14	39			
			12				

	Time	120	240	480	720	1200	1800
12.5	0	1.1	3.6	14	25	54	80
		1.1				50	
12.5	50	5.2	21	39	60	104	164
			15				
12.5	87.5	4.3	15	30	53	101	221
			12		52		164
			11				

Table 4-b

Quantities of 1-C_4H_8 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 853K

C_2H_4	CH_4 \ Time	30	60	120	240	360
50	0	1.8	4.9	16	34	55
			4.5		41	66
			4.9			
50	200	0.5	1.7	4.4	13	22
			1.5			
50	350	0.5	1.1	3.3	9.1	15
			1.0			

	Time	60	120	240	360	600	900
25	0	1.0	2.6	13	13	21	29
		1.5	4.7	12	20		34
							33
25	100	0.4	1.4	3.4	6.2	9.5	17
25	175	0.3	0.8	2.8	3.8	6.9	11
			0.9	2.1			
			0.7				

	Time	120	240	480	720	1200	1800
12.5	0	1.3	3.4	7.1	8.2	8.2	9.0
		1.3				11	
12.5	50	0.4	1.4	2.3	3.3	4.9	6.1
			1.0				
12.5	87.5		0.4	1.2	1.9	3.2	5.9
			0.4		1.8		4.4

Table 4-c

Quantities of 1,3-C_4H_6 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 853K

C_2H_4	CH_4	Time 30	60	120	240	360
50	0	2.4	6.8 6.4 6.9	22	51 64	88 113
50	200	2.2	5.5 5.3	15	43	80
50	350	2.4	5.4 4.4	14	40	69

	Time	60	120	240	360	600	900
25	0	1.7 2.6	4.7 8.8	27 25	28 45	58	94 120 116
25	100	2.1	6.8	17	33	63	101
25	175	2.3	5.2 5.7 5.0	19 15	27	52	90

	Time	120	240	480	720	1200	1800
12.5	0	3.6 3.4	10	28	41	65 63	84
12.5	50	2.8 7.8	11	20	32	52	79
12.5	87.5	1.7	6.1 5.3	13	23 22	42	86 66

Table 4-d

Quantities of C_2H_6 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 774K

C_2H_4	CH_4	1-C_4H_8	Time	150	300	600	1200	1800
50	0	0		0.5	0.8	1.7 1.9	4.3	8.9
0	0	2			2.2	4.5	9.6	15
0	400	1.65			2.9	5.7	13	19
50	0	2			32	63	129	189
50	150	1.65			46	95	185	273
50	400	1.65			64	124	264	

			Time	300	600	1200	1800	2400	3600
25	0	0		0.3	0.6 0.5	1.1		3.4*	6.8
0	0	1		0.7	1.7	3.4	5.2		9.8
0	200	0.8			2.6	5.0		9.6	14
25	0	1			21	42		77	121 124
25	75	0.8			34	67		134	178
25	200	0.8			45	92		174	260

* 2520 seconds instead of 2400.

Table 5-a

Quantities of C_3H_6 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 774K

C_2H_4	CH_4	1-C_4H_8	Time	150	300	600	1200	1800
50	0	0		1.4	2.3	5.4 5.3	12	26
0	0	2			20	43	90	131
0	400	1.65			23	47	93	131
50	0	2			98	193	378	514
50	150	1.65			93	183	352	493
50	400	1.65			100	195	386	

			Time	300	600	1200	1800	2400	3600
25	0	0		0.4	0.9 0.9	2.0		6.1*	12
0	0	1		7.4	18	35	55		99
0	200	0.8			24	48		89	122
25	0	1			78	150		258	367 375
25	75	0.8			76	144		272	347
25	200	0.8			76	151		281	377

* 2520 seconds instead of 2400.

Table 5-b

Quantities of 1,3-C_4H_6 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 774K

C_2H_4	CH_4	1-C_4H_8	Time	150	300	600	1200	1800
50	0	0			0.7	1.1 1.7	3.2	6.2
0	0	2			19	37	74	98
0	400	1.65			22	44	86	116
50	0	2			28	53	89	108
50	150	1.65			30	51	82	101
50	400	1.65			23	42	74	

			Time	300	600	1200	1800	2400	3600
25	0	0				0.9		2.6*	5.0
0	0	1			13		42		70
0	200	0.8			23	46		80	105
25	0	1			26	46		74	87 85
25	75	0.8			24	43		71	80
25	200	0.8			23	43		68	85

* 2520 seconds instead of 2400.

Table 5-d

Quantities of C_2H_6 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 853K

C_2H_4	CH_4	1-C_4H_8	Time	30	60	120	240	360
50	0	0		2.0	5.7	19	45	88
					5.3		56	107
					5.5			
50	0	1.9			118	227	395	588*
50	400	1.6			239	467	829	

			Time	60	120	240	360	600	900
25	0	0		1.1	3.1	18	20	44	100
				1.8	5.7	16	30		80
									96
25	0	0.95		34	65	125	164**		
25	200	0.8			159	274	363	533	

* 390 seconds instead of 360.

** 380 seconds instead of 360.

Table 6-a

Quantities of C_3H_6 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 853K

C_2H_4	CH_4	1-C_4H_8	Time	30	60	120	240	360
50	0	0		1.6	4.5	17	44	94
					4.4		54	122
					4.3			
50	0	1.9			513	865	1240	1530*
50	400	1.6			443	787	1240	

			Time	60	120	240	360	600	900
25	0	0		0.8	2.2	16	17	47	95
				1.2	4.0	14	28		124
									127
25	0	0.95		239	413	635	713**		
25	200	0.8			379	605	727	935	

* 390 seconds instead of 360.

** 380 seconds instead of 360.

Table 6-b

Quantities of 1,3-C_4H_6 formed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 853K

C_2H_4	CH_4	1-C_4H_8	Time	30	60	120	240	360
50	0	0		2.4	6.8	22	51	88
					6.4		64	113
					6.9			
50	0	1.9			244	369	475	511*
50	400	1.6			187	305	415	

			Time	60	120	240	360	600	900
25	0	0		1.7	4.7	27	28	58	94
				2.6	8.8	25	45		120
									116
25	0	0.95		118	193	285	286**		
25	200	0.8			170	240	269	303	

* 390 seconds instead of 360.

** 380 seconds instead of 360.

Table 6-d

Quantities of 1-C_4H_8 consumed (in millitorr in a 210 cm^3 reactor), as a function of pyrolysis time (second).

T = 774K

C_2H_4	CH_4	1-C_4H_8	Time	300	600	1200	1800
0	0	2		80	130	250	420
0	400	1.65		70	110	260	380
50	0	2		50	200	310	460
50	150	1.65			70	230	330
50	400	1.65		50	170	250	

			Time	600	1200	1800	2400	3600
0	0	1		40	170	190		360
0	200	0.8			40		140	230
25	0	1		80	150			360
25	75	0.8			50		150	230
25	200	0.8			75		165	225

Table 5-c

Quantities of 1-C_4H_8 consumed (in a 210 cm^3 reactor),
as a function of pyrolysis time (second).
T = 853K

C_2H_4	CH_4	1-C_4H_8	Time	60	120	240	360	390	
50	0	1.9		500	840	1220		1450	
50	400	1.6		410	630	920			
			Time	60	120	240	360	380	600
25	0	0.95		220	390	630		720	
25	200	0.8			260	420	520		620

Table 6-c

Initial rate of formation of products (10^{-12} mole.cm^{-3}.s^{-1})

T=774K

C_2H_4 (Torr)	CH_4 (Torr)	C_2H_6	C_3H_6	1-C_4H_8	1,3-C_4H_6
200	0	0.5	5.8	1.2	0.4
200	20	0.5	5.2	1.0	0.4
200	100	1.0	5.8	1.2	0.4
200	200	1.0	5.6	0.9	0.3
100	0	0.2	0.9	0.3	0.2
100	100	0.3	1.0	0.2	0.1
100	200	0.6	1.5	0.3	0.2
100	300	0.6	1.2	0.2	0.2
50	0	0.04	0.13	0.06	0.04
50	50	0.11	0.22	0.06	------
50	150	0.16	0.24	0.04	0.03
50	250	0.24	0.34	0.03	0.04
50	400	0.41	0.50	0.04	0.06
25	0	0.01	0.02	0.01	0.01
25	25	0.03	0.04	0.01	0.01
25	75	0.05	0.06	0.01	------
25	125	0.07	0.09	0.01	0.01
25	200	0.10	0.13	0.01	------
14	186	0.05	0.07	0.003	0.01
14	286	0.09	0.12	0.003	0.01

Table 7

Initial rate of formation of products (10^{-12} mole.cm^{-3}.s^{-1})

T=824K

C_2H_4 (Torr)	CH_4 (Torr)	C_2H_6	C_3H_6	1-C_4H_8	1,3-C_4H_6
50	0	0.25	0.30	0.25	0.25
50	200	0.60	0.80	0.10	0.20
50	350	1.25	1.60	0.14	0.45
25	0	0.07	0.05	0.07	0.07
25	100	0.30	0.37	0.05	0.16
25	175	0.40	0.50	0.04	0.17
12.5	0	0.01	0.01	0.01	0.03
12.5	50	0.08	0.13	0.01	0.06
12.5	87.5	0.14	0.27	0.01	0.08

Table 8

Initial rate of formation of products (10^{-12} mole.cm^{-3}.s^{-1})

T=853K

C_2H_4 (Torr)	CH_4 (Torr)	C_2H_6	C_3H_6	1-C_4H_8	1,3-C_4H_6
50	0	1.0	0.7	0.8	1.3
50	200	1.8	2.5	0.3	1.2
50	350	2.0	3.0	0.2	1.1
25	0	0.3	0.2	0.25	0.4
25	100	0.6	1.0	0.10	0.5
25	175	0.7	1.2	0.06	0.5
12.5	0	0.15	0.08	0.13	0.30
12.5	50	0.25	0.50	0.04	0.25
12.5	87.5	0.20	0.50	0.02	0.20

Table 9

Initial rate of formation of products (10^{-12} mole.cm^{-3}.s^{-1})

T=774K

C_2H_4 (Torr)	1-C_4H_8 (Torr)	CH_4 (Torr)	C_2H_6	C_3H_6	1,3-C_4H_6
50	0	0	0.04	0.13	0.04
0	2	0	0.15	1.5	1.3
50	2	0	2.2	6.8	2.1
50	1.7	150	3.2	6.8	2.2
50	1.7	400	4.4	7.0	1.7
25	0	0	0.01	0.02	0.01
0	1	0	0.06	0.50	0.45
25	1	0	0.75	2.8	1.0
25	0.85	75	1.2	2.8	1.0
25	0.85	200	1.6	2.7	0.9

Table 10

Initial rate of formation of products (10^{-12} mole.cm^{-3}.s^{-1})

T=853K

C_2H_4 (Torr)	1-C_4H_8 (Torr)	CH_4 (Torr)	C_2H_6	C_3H_6	1,3-C_4H_6
50	0	0	1.0	0.7	1.3
50	1.9	0	39	180	90
50	1.6	400	76	150	65
25	0	0	0.3	0.2	0.4
25	0.95	0	11.5	85	54
25	0.8	200	28	70	32

Table 11

Volume

2

MECHANISMS FOR THE HOMOGENEOUS, THERMAL CONVERSION OF METHANE TO ETHANE AND OTHER SATURATED HYDROCARBONS

PART 2

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MICROMEDIA

EXPERIMENTAL

The apparatus, gases and experimental procedure technique were identical to those described in our previous report.

The sampling and analytical techniques were also the same but the following additions have been made.

Sampling technique: A 0.15 ml loop has been built in order to analyze quantitatively C_2H_4. It was equipped at both ends, as the 5ml loop previously described, with 1/8" Whitey ball valve and 1/8" tubing. This small volume loop was necessary because the quantity of ethylene injected with a 5ml loop in the Phenylisocyanate column was too large to be analyzed.

Silicagel column analysis: In addition to the analysis of ethane, this column was also used to analyze benzene and toluene in the experiments where the conversion of ethylene was important. The column has been calibrated for benzene. The sensitivity for toluene has been taken equal to that of benzene multiplied by 7/6 (ratio of the number of carbon atoms in the molecules). The peaks corresponding to benzene and toluene may also contain some other C_6 or C_7 compounds such as cyclohexene or cyclohexadiene. No attempt was made to differentiate those compounds.

Phenylisocyanate column analysis: The following sensitivities have been taken arbitrarily for the quantification of acetylene, allene, 2-butene and a C_5 compound eluted after 120 min. For acetylene, allene and 2-butene we have chosen to take sensitivities (area per unit of compound) respectively equal to those of ethane, propylene and 1-butene. The sensitivity of the C_5 compound was taken equal to that of 1-butene multiplied by 5/4 (ratio of the number of carbon atoms in the molecules).

Those sensitivities were necessary in order to calculate the total production of hydrocarbons and to compare with the quantity of ethylene consumed.

RESULTS AND DISCUSSION

Summary

Twenty series of experiments have been done at the following three temperatures: 925, 974 and 1023K. Eighteen series have been done in order to study the initial stage of the reaction. Two series have been done in order to study the behavior at long pyrolysis times and to compare the quantities of products formed with the quantity of ethylene consumed. A summary is given in table 1.

Contrary to the case of the experiments done at lower temperatures, described in our previous report, it was not possible in most cases to calculate initial rates of formation of the products, the reaction being too fast. Therefore we do not report here any initial rates.

Pyrolysis of methane itself under the conditions of the present study produced negligible amount of products.

Study of the initial stage of the reaction

Six series of experiments have been done at the three temperatures: 925, 974 and 1023K. For each run, the amounts of ethane, acetylene, propylene, 1-butene and 1,3-butadiene produced were determined. Results are reported in tables 2 to 14.

925K

Results of the experiments done at 925K are reported in tables 2 to 6. Six series of experiments have been done with 25 or 12.5 Torr of ethylene and 0 to 400 Torr of methane.

The main compounds produced from pure ethylene are in order of importance: 1,3-butadiene, propylene, ethane, methane, acetylene and 1-butene. When methane is added to ethylene, propylene becomes the most important product. The addition of methane has the following two main influences on the products of the reaction: it increases the production of propylene and it sharply decreases the production of all the other compounds. We have reported in figure 1 the initial ratio (extrapolated at zero time), X/C_3H_6, where X is a product, plotted as a function of the quantity of methane in the initial mixture. This figure clearly shows the sharp decreases of ethane, 1-butene, acetylene and 1,3-butadiene relative to propylene.

974K

Results of the experiments done at 974K are reported in tables 7 to 10. Six series of experiments have been done with 12.5 or 6.25 Torr of ethylene and 0 to 200 Torr of methane. The main products formed from pure ethylene are in order of importance: 1,3-butadiene, propylene or acetylene, methane, ethane and 1-butene. When methane is added in the initial mixture, propylene becomes the most important product.

The addition of methane to ethylene has the following two main consequences: it increases the production of propylene and decreases the production of the other compounds.

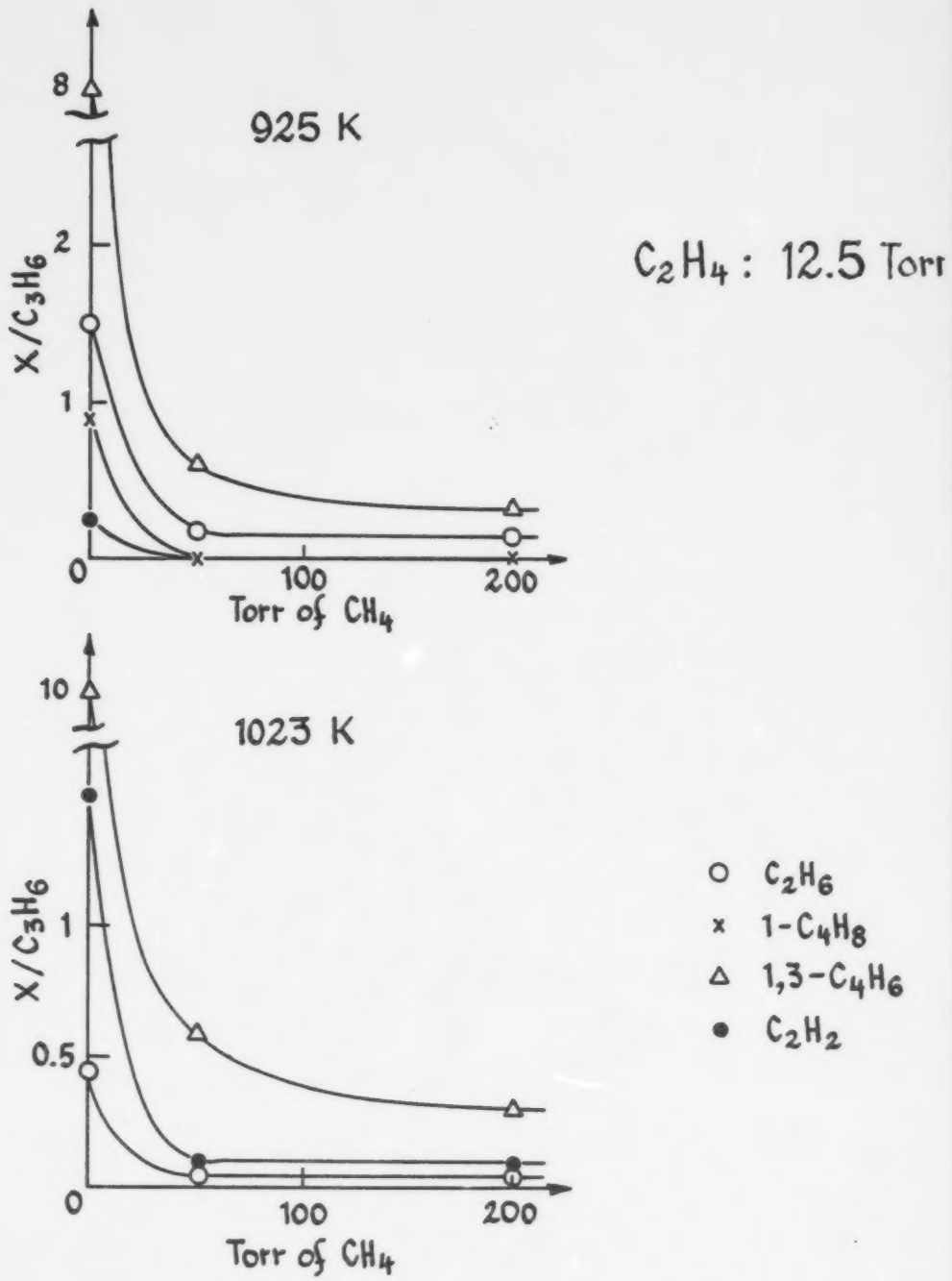

925 K
C_2H_4 : 12.5 Torr
8
2
1
0
X/C_3H_6
100
200
Torr of CH_4
1023 K
10
1
0.5
0
X/C_3H_6
100
200
Torr of CH_4
○ C_2H_6
× $1\text{-}C_4H_8$
△ $1,3\text{-}C_4H_6$
● C_2H_2

FIGURE 1

1023K

Results of the experiments done at 1023K are reported in tables 11 to 14. Six series of experiments have been done with 12.5 or 6.25 Torr of ethylene and 0 to 200 Torr of methane. Results obtained for the experiments done with 12.5 Torr of ethylene are reported in figures 2 and 3.

The main compounds produced from pure ethylene are in order of importance: 1,3-butadiene, acetylene, methane, propylene, ethane and 1-butene. As in the experiments done at 925 and 974K, the addition of methane increases the production of propylene and decreases the production of the other compounds. Figure 1 again shows clearly that the production of propylene is greatly favoured by the presence of methane in the initial mixture.

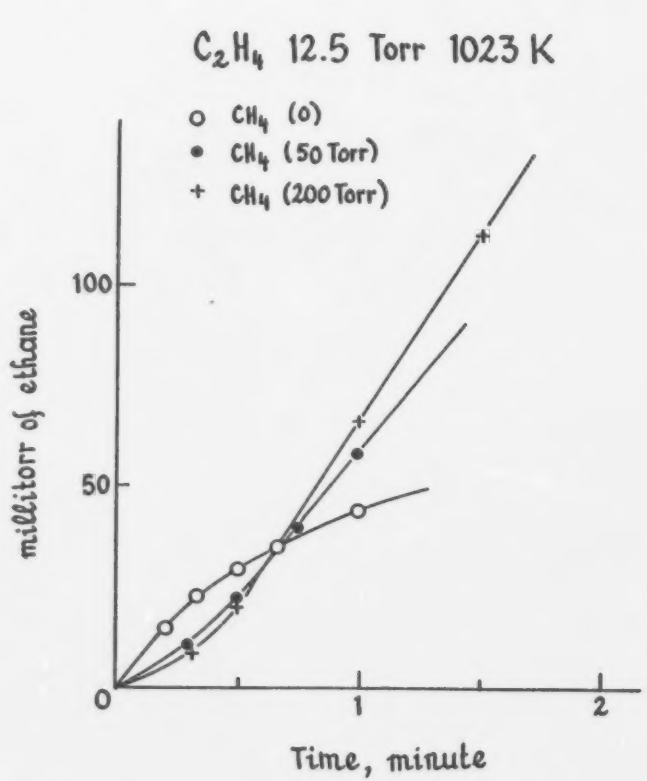
Discussion of the results of the study of the initial stage of the reaction

The initial stage of the pyrolysis of ethylene-methane mixtures has been studied at six temperatures, 774, 824, 853, 925, 974 and 1023K. The changes observed in the product distribution at these temperatures are summarized as follows.

Pure ethylene pyrolysis

When ethylene was pyrolyzed at the lowest temperature studied, propylene was the main compound initially produced followed by 1-butene. They represented respectively up to 70 and 18% of the products (calculated as % of the ethylene transformed). When the pressure of ethylene was lowered at that temperature, the relative importance of propylene and 1-butene decreased and that of ethane and 1,3-butadiene increased.

As the temperature is raised from 774 to 1023K the following trends were


C_2H_4 12.5 Torr 1023 K
○ CH_4 (0)
● CH_4 (50 Torr)
+ CH_4 (200 Torr)
millitorr of ethane
100
50
0
1
2
Time, minute

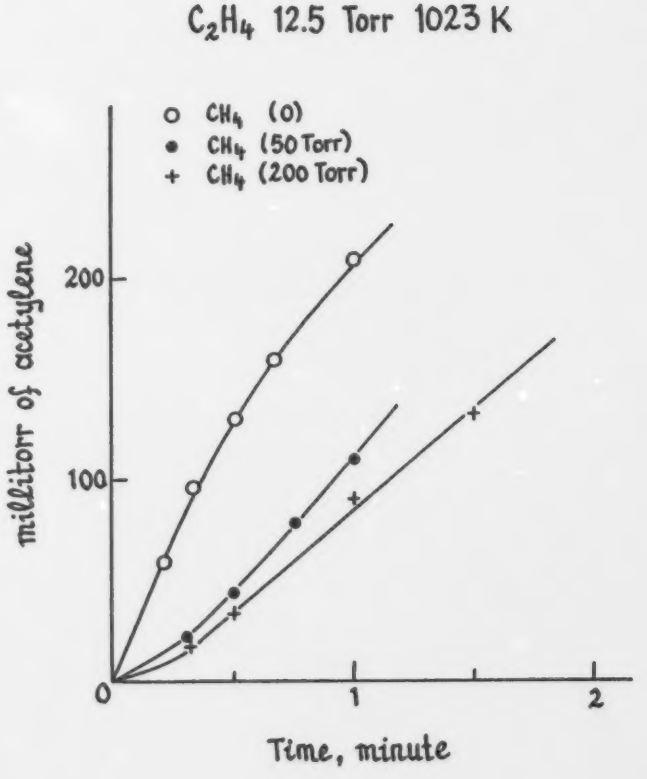
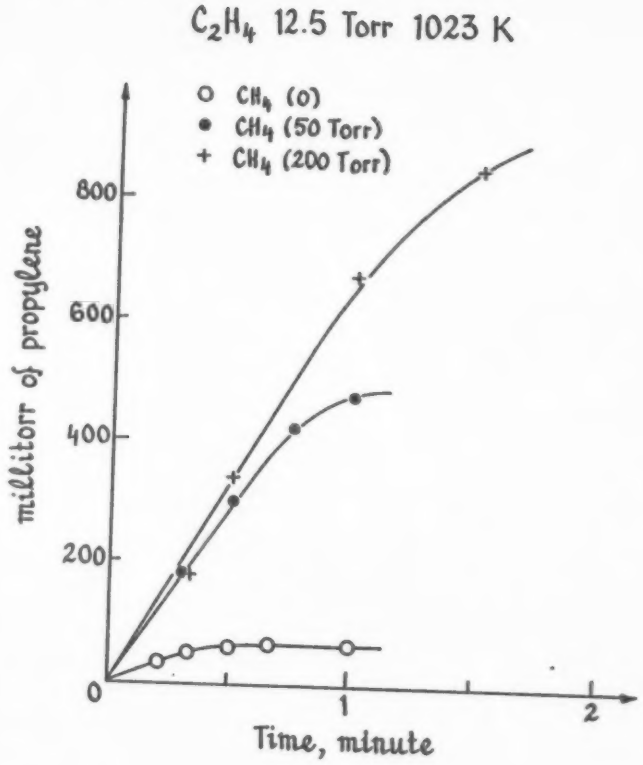

C_2H_4 12.5 Torr 1023 K
○ CH_4 (0)
● CH_4 (50 Torr)
+ CH_4 (200 Torr)
millitorr of acetylene
200
100
0
1
2
Time, minute

FIGURE 2


C_2H_4 12.5 Torr 1023 K
○ CH_4 (0)
● CH_4 (50 Torr)
+ CH_4 (200 Torr)
millitorr of propylene
800
600
400
200
0
1
2
Time, minute

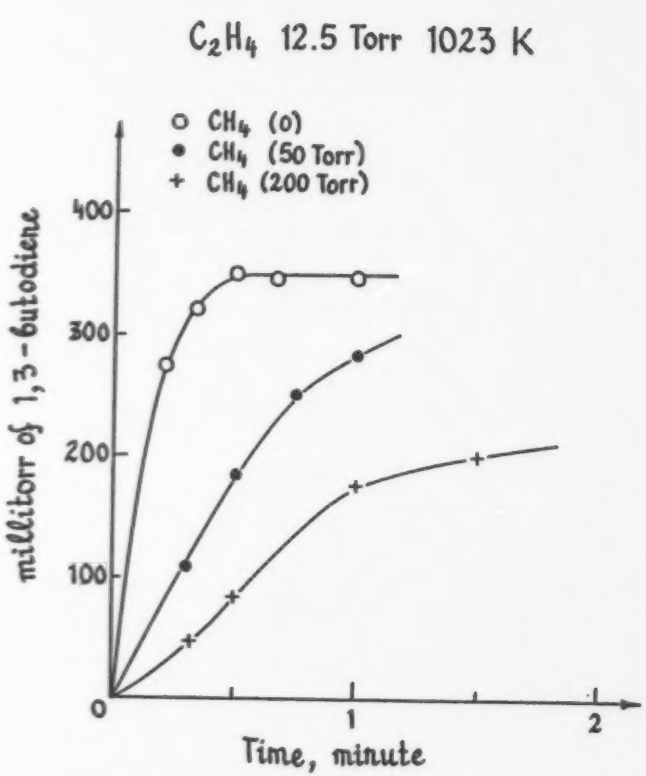

C_2H_4 12.5 Torr 1023 K
○ CH_4 (0)
● CH_4 (50 Torr)
+ CH_4 (200 Torr)
millitorr of 1,3-butodiene
400
300
200
100
0
1
2
Time, minute

FIGURE 3

observed:

(1) the production of acetylene, negligible at 774K becomes more and more important and is second in importance to that of 1,3-butadiene at 1023K.

(2) the production of 1-butene, second in importance to that of propylene at 774K becomes less and less important and negligible at 974 and 1023K.

(3) the production of propylene relative to that of acetylene or 1,3-butadiene decreases when the temperature is increased.

(4) 1,3-butadiene, a minor compound at 774K, becomes the most important product at 1023K

At the highest temperature studied, 1023K, the two main initial products, 1,3-butadiene and acetylene, represent respectively up to 80 and 10% of the products.

Ethylene-Methane pyrolysis

The addition of increasing quantities of methane to ethylene increases the absolute production of ethane at 774, 824 and 853K but decreases it at 925, 974 and 1023K. At all temperatures the absolute production of propylene is increased by the presence of methane as a reactant.

In figure 4 and 5 the ratios C_2H_6/C_3H_6 and $1,3\text{-}C_4H_6/C_3H_6$ are shown as a function of the pressure of methane at the different temperatures studied. Those figures clearly show that the presence of methane favored the production of propylene relative to that of ethane and 1,3-butadiene. The behavior of 1-butene is identical in that respect to that of 1,3-butadiene. As the temperature and pressure of methane are increased the relative production of propylene becomes more and more important. At the highest temperature and pressure studied, it accounts for up to 85% (by weight) of the products.

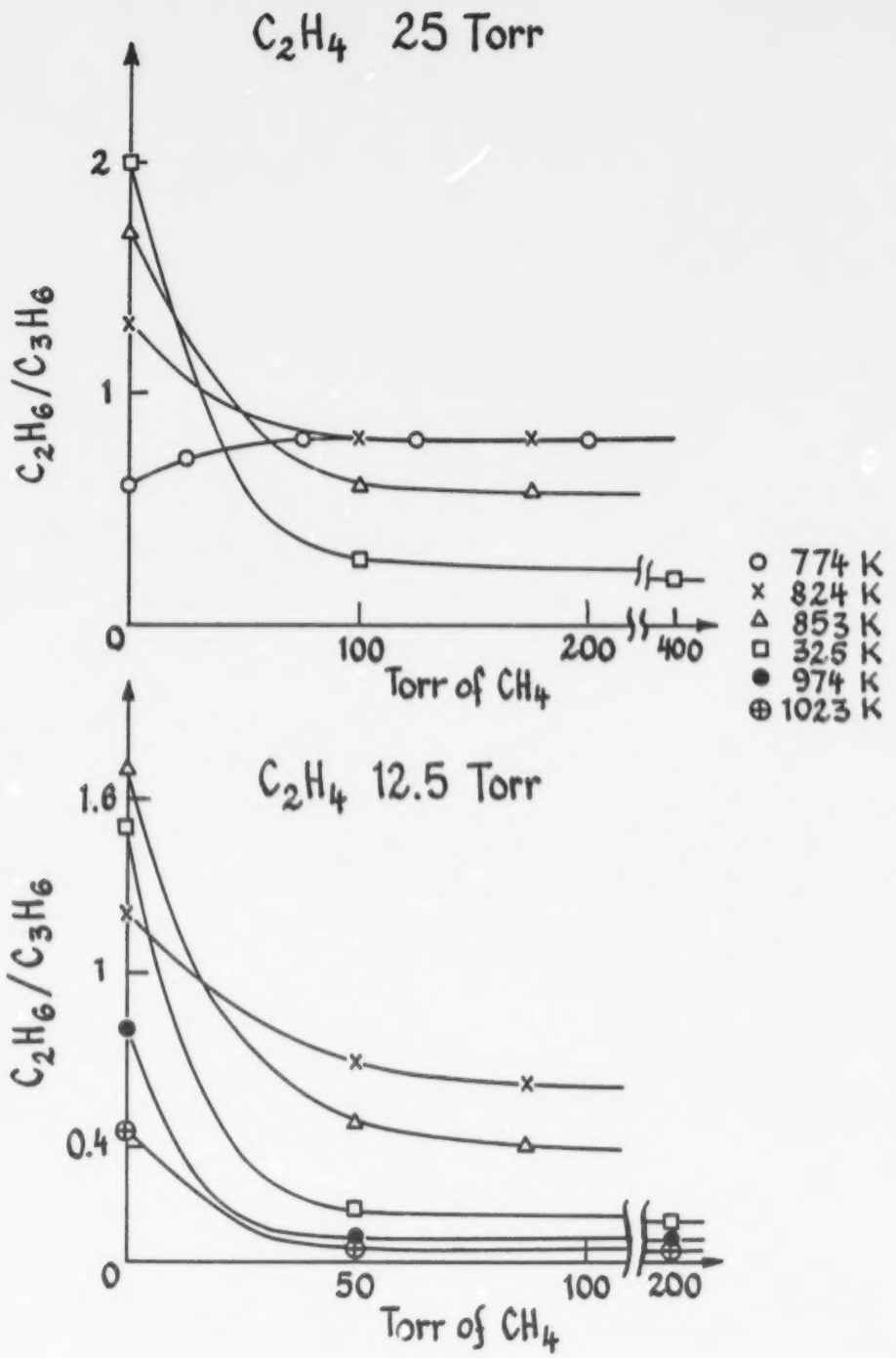

C_2H_4 25 Torr
C_2H_6/C_3H_6
2
1
0
100
200
400
Torr of CH_4
○ 774 K
× 824 K
△ 853 K
□ 325 K
● 974 K
⊕ 1023 K
C_2H_4 12.5 Torr
C_2H_6/C_3H_6
1.6
1
0.4
0
50
100
200
Torr of CH_4

FIGURE 4

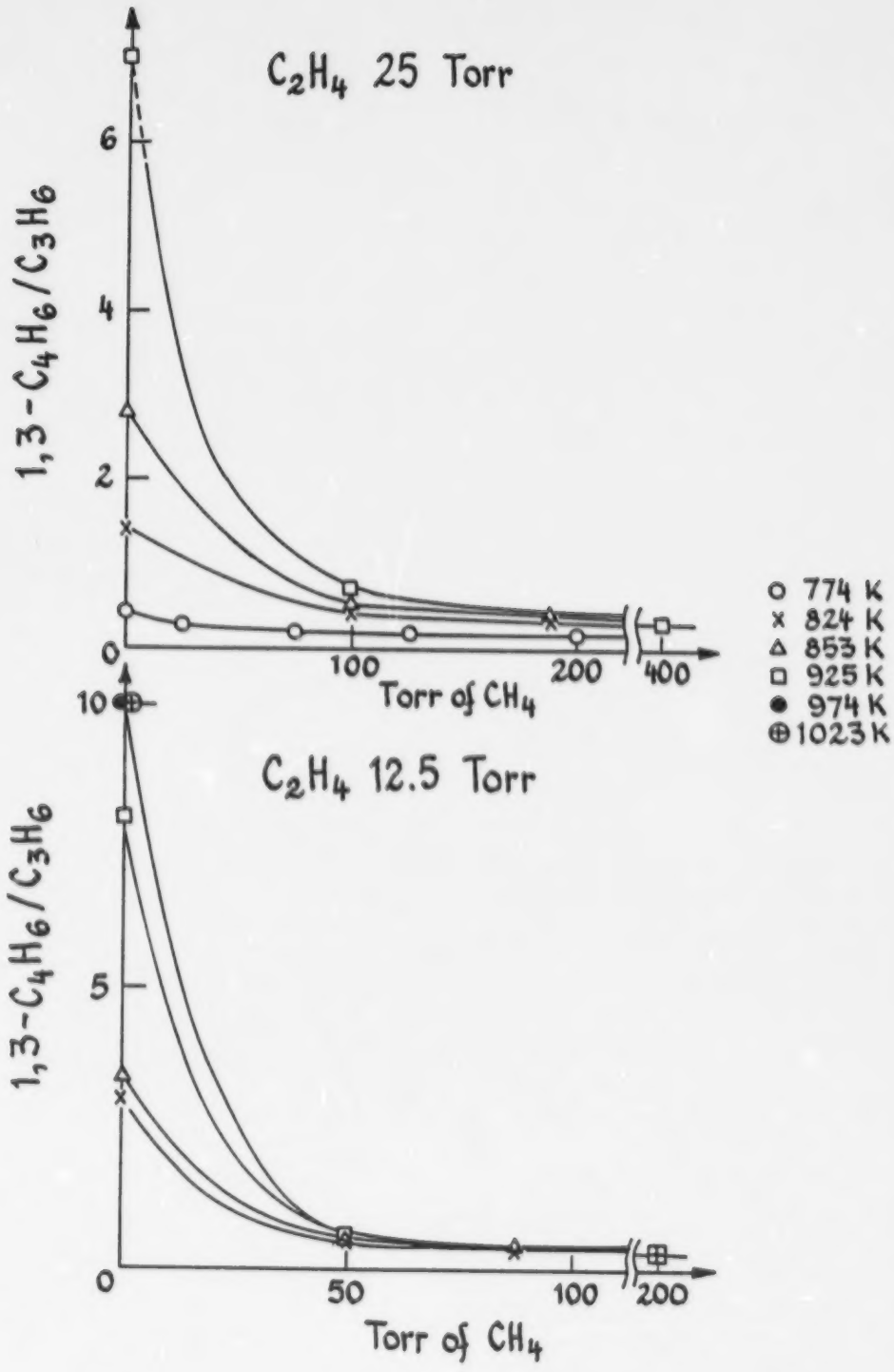

C_2H_4 25 Torr
1,3-C_4H_6/C_3H_6
6
4
2
0
100
200
400
Torr of CH_4
○ 774 K
× 824 K
△ 853 K
□ 925 K
● 974 K
⊕ 1023 K
C_2H_4 12.5 Torr
1,3-C_4H_6/C_3H_6
10
5
0
50
100
200
Torr of CH_4

FIGURE 5

The mechanism of the reaction

The change in the product distribution in the higher temperature region shows that decomposition of radicals by C-H bond fission is now the most important pathway, in contrast to the decomposition by C-C bond breaking which occured in the lower temperature region. The key to this conclusion is the appearance of acetylene, which is formed by dissociation of the vinyl radical. By comparison, other radicals may undergo C-H bond breaking and the following reactions would become important routes to formation of propylene and butadiene.

[1] C_2H_3 -----> $C_2H_2 + H$

[2] C_2H_5 -----> $C_2H_4 + H$

[3] $CH_3 + C_2H_4$ -----> C_3H_7 -----> $C_3H_6 + H$

[4] $C_2H_3 + C_2H_4$ -----> C_4H_7 -----> $C_4H_6 + H$

As mentioned, butadiene and acetylene are the major products at the higher temperature, 1023K.

On addition of methane the only product whose rate of formation is increased is propylene. Ethane, acetylene and butadiene decreased in the presence of methane. This suggests that reactions [1] and [2] may be equilibrated and addition of methane removes hydrogen atoms, converting them to methyl radicals.

[5] $H + CH_4$ -----> $H_2 + CH_3$

The concentration of methyl radicals is thus increased relative to the other radicals, leading to an increase in the rate of formation of propylene at the expense of the other products. These effects are illustrated by the figures 4 and 5 showing the ratios C_2H_6/C_3H_6 and C_4H_6/C_3H_6 at the various temperatures as a function of the pressure of methane. It is also evident from these figures that the ratios tend toward a constant value, suggesting that certain equilibria may be established at these temperatures.

The balance between products and ethylene consumed

Two series of experiments have been done at 974 and 1023K in which all the products, up to C_7, and the remaining ethylene have been determined quantitatively at different times of pyrolysis. These series, done with mixtures containing 6.5 Torr of ethylene and 356 Torr of methane, have been done in order to determine the extent of the incorporation of methane into the products of the reaction.

The results are reported in tables 15 and 16 and are plotted in figures 6 and 7. The mixture has the same behavior at 974 and 1023K, the only major difference being the time scale. The main initial product is propylene. As the reaction goes on, propylene reaches rapidly a maximum and then seems to decrease to a plateau value. Ethane and acetylene, though produced in smaller quantities , have the same behavior. The main product at long pyrolysis time is benzene. Toluene is also produced but in much smaller quantities. At both 974 and 1023K the consumption of ethylene is proportional to the time of pyrolysis, at least until 1/3 is consumed.

The average consumption of ethylene is compared to the average total quantity of product (normalized to mol of ethylene) as a function of time in figure 8. If all the products were derived from ethylene the two sets of data would be coincident. Clearly substantial product is produced by reaction of methane. The results also show that the incorporation of methane into products is a maximum at a moderately low conversion of ethylene and at longer times of reaction the products are converted to higher molecular weight products (probably carbon) which are not analyzed. Efficient conversion of methane to low molecular weight hydrocarbons is therefore critically dependent on the extent of the reaction.

The maximum conversion of methane into propylene occurs at both temperatures at a consumption of about one torr of ethylene. The comparison

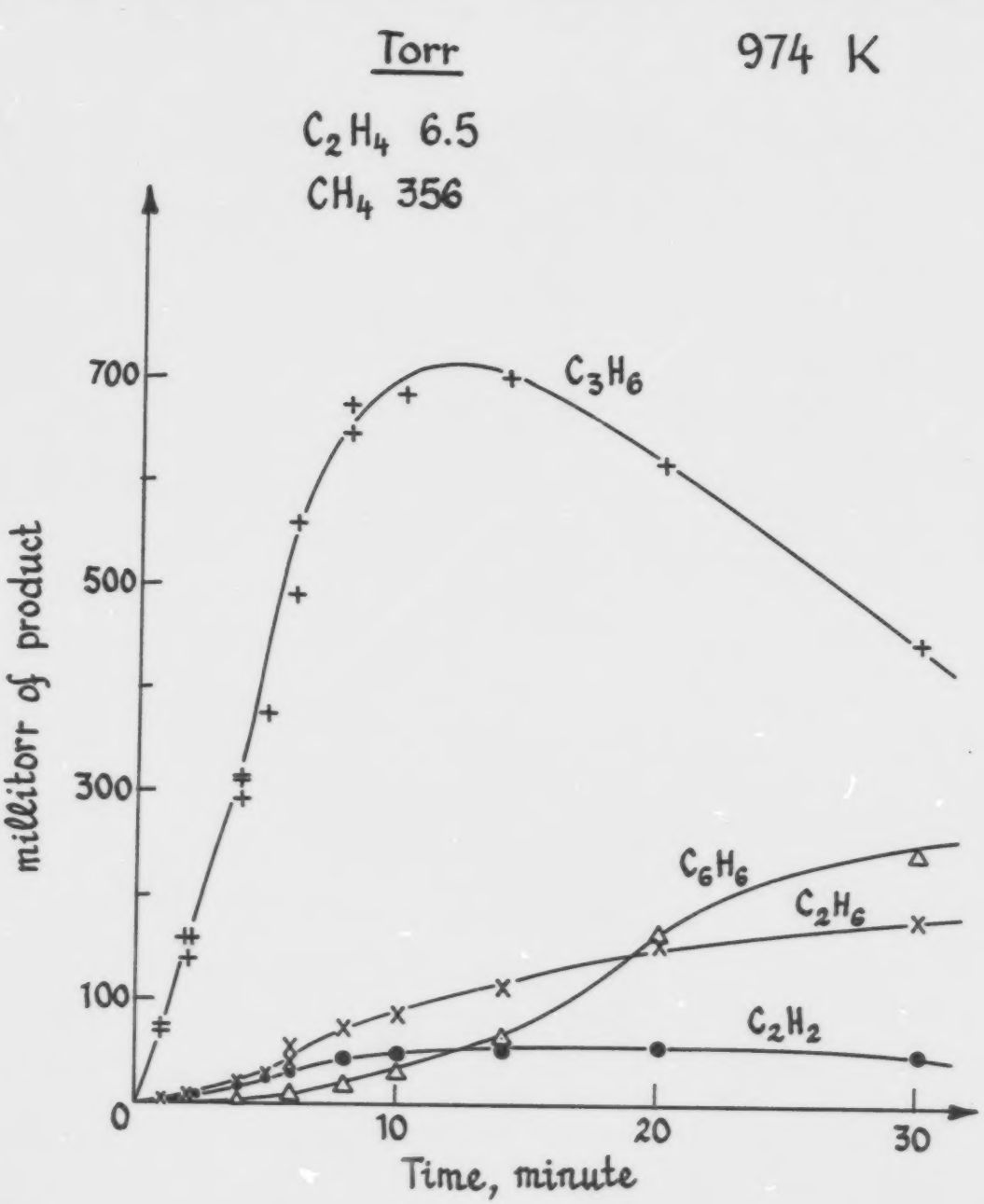

Torr
974 K
C_2H_4 6.5
CH_4 356
millitorr of product
700
500
300
100
0
C_3H_6
C_6H_6
C_2H_6
C_2H_2
10
20
30
Time, minute

FIGURE 6

Torr

C_2H_4 6.5

CH_4 356

1023 K

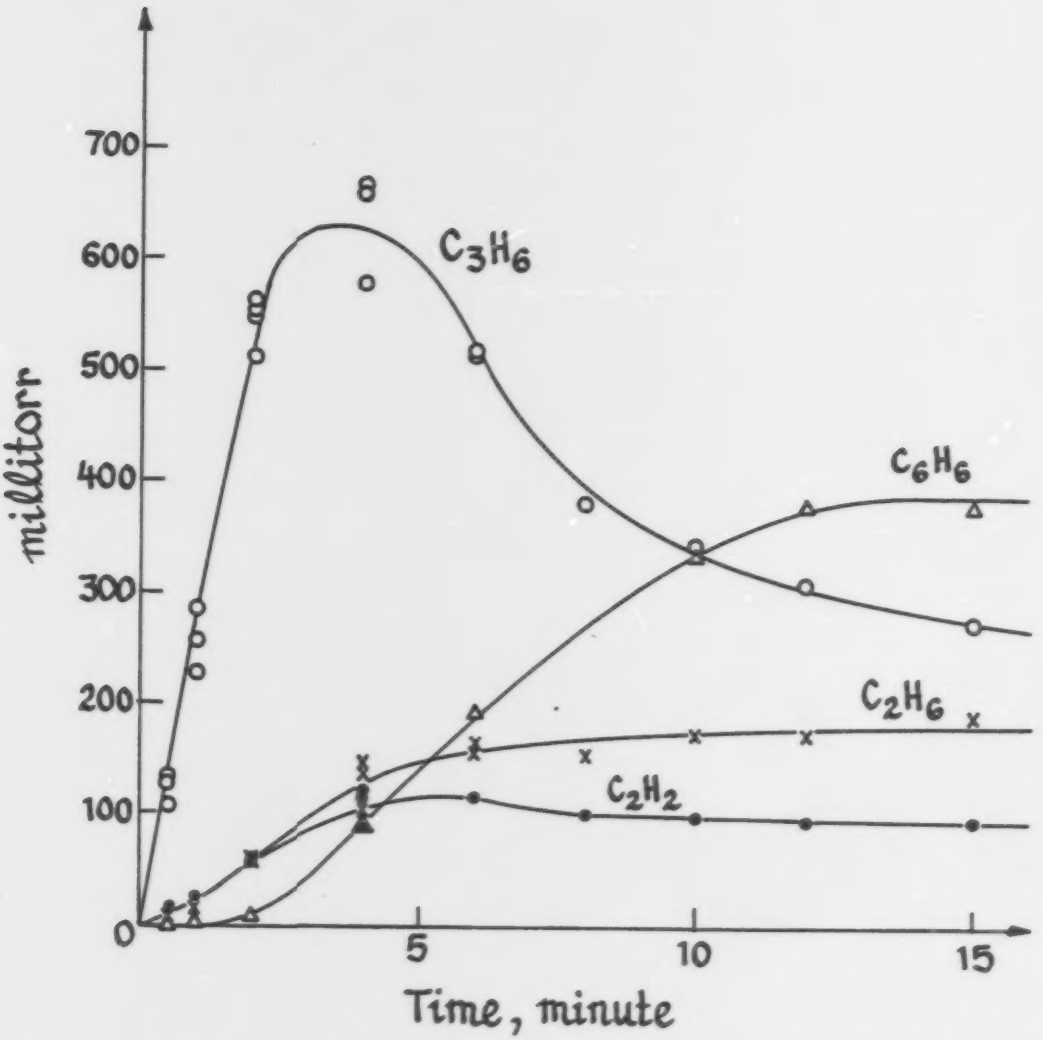


FIGURE 7

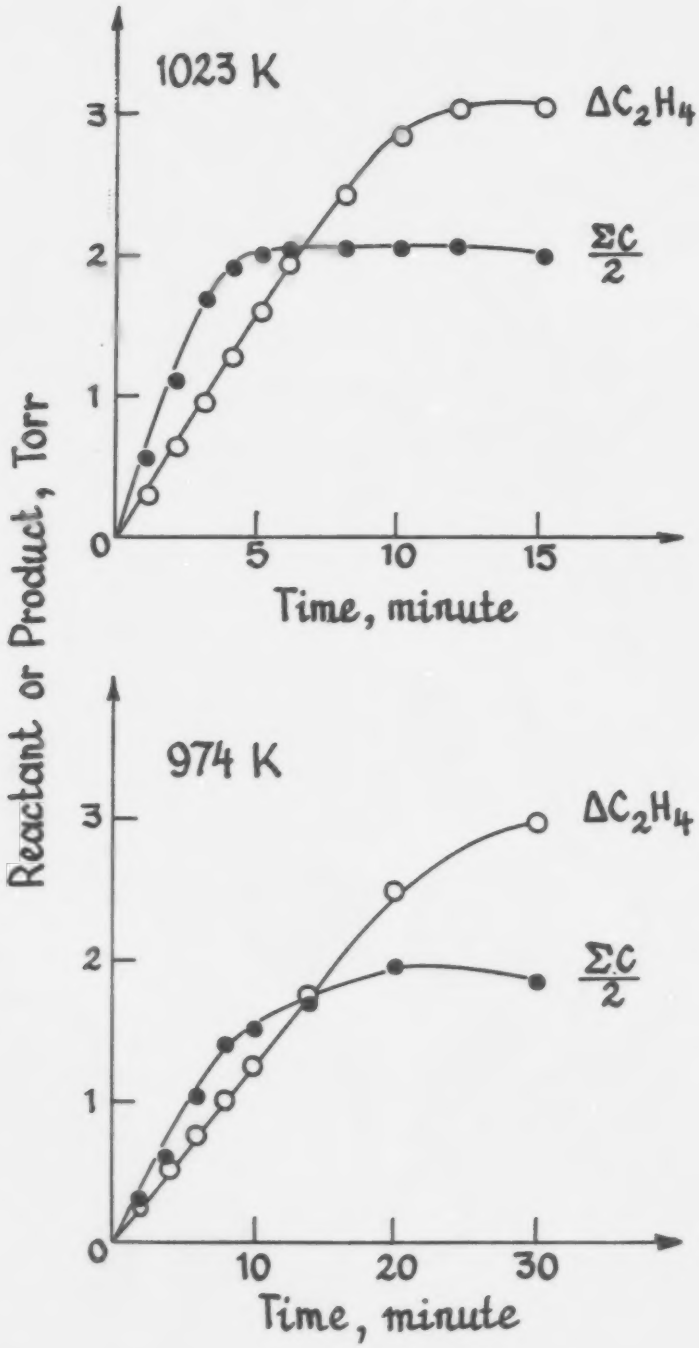

1023 K
ΔC_2H_4
$\frac{\Sigma C}{2}$
Reactant or Product, Torr
Time, minute
974 K
ΔC_2H_4
$\frac{\Sigma C}{2}$
Time, minute

FIGURE 8

between the ethylene consumed and the methane reacted at this stage of the reaction is summarized in the following table.

	974K	1023K
C_2H_4 consumed	1 Torr	1 Torr
Time of reaction	8 min	3 min
Total C in product	2.8 Torr	3.4 Torr
C from methane	0.8 Torr	1.4 Torr
% conversion $C2H_4$	15	15
% conversion CH_4	0.11	0.21
% conversion CH_4/sec	$2.3\ 10^{-4}$	$1.2\ 10^{-3}$

These results show that at 974K 0.8 mol of methane are consumed for every mol of ethylene while at 1023K 1.4 mol of methane are consumed for every mol of ethylene. The percentage conversion of methane appears very low because of the large excess of methane used in these experiments.

It is of interest to contrast the results of the methane conversion sensitized by ethylene and sensitized by catalytic oxidation. In the latter reaction only ethane and ethylene are major products and propylene is usually negligible. In view of the major production of propylene in the present stystem the question arises as to why propylene is not formed in the oxidative coupling of methane, since ethylene is present as a product in the latter reaction and therefore radical addition could be expected. The answer may lie in the role of oxygen. Consider the following homogeneous reactions of the methyl radical which may occur in both systems.

[6] $CH_3 + CH_3 \text{ -----> } C_2H_6$

[7] $CH_3 + O_2 \text{ -----> } CH_3O_2 \text{ -----> } CH_2O + OH$

[8] $CH_3 + C_2H_4 \text{ -----> } C_3H_7 \text{ -----> } C_3H_6 + H$

Reaction [7] is considerably faster than reaction [8] and only a small quantity of oxygen would be sufficient to compete successfully with reaction [8]. In the presence of oxygen addition of methyl radicals to ethylene can be kept low.

In summary, at temperatures in the region of 1000K ethylene is an efficient sensitizer for the conversion of methane to propylene. The main advantage of the use of a hydrocarbon sensitizer is that no methane is lost to carbon monoxide or carbon dioxide.

Composition of the C_2H_4 - CH_4 mixtures
pyrolyzed at 925, 974 and 1023K.

	Temperature (K)		
	925	974	1023
Ethylene (Torr)		Methane (Torr)	
25	0, 100, 400		
12.5	0, 50, 200	0, 50, 200	0, 50, 200
6.25		0, 25, 100	0, 25, 100
6.5		356	356

Table 1

Quantities of C_2H_6 formed (in millitorr in a 210cm^3 reactor), as a function of pyrolysis time (second).

T = 925K

		Time (second)					
		18	30	45	60	90	120
C_2H_4	CH_4	C_2H_6 (millitorr)					
25	0	10	23 22	39	51		
25	100	6.3	16	28	39	73	
25	400		12		26		68

		Time (second)				
		30	60	90	120	180
C_2H_4	CH_4	C_2H_6 (millitorr)				
12.5	0	5.8	13 12	19	25	
12.5	50	2.7	6.5		16	27
12.5	200	2.1	4.4		12	17

Table 2

Quantities of C_2H_2 formed (in millitorr in a 210cm^3 reactor), as a function of pyrolysis time (second).

T = 925K

		Time (second)					
		18	30	45	60	90	120
C_2H_4	CH_4	C_2H_2 (millitorr)					
25	0	1.3	3.2 3.2	6.0	8.0		
25	100	0.6	1.3	2.5	3.2	6.8	
25	400		1.1		2.4		5.5

		Time (second)				
		30	60	90	120	180
C_2H_4	CH_4	C_2H_2 (millitorr)				
12.5	0	1.4	3.7 3.5	5.9	8.5	
12.5	50	<0.3	<0.3		0.6	5.1
12.5	200	0.3	0.8		2.0	3.2

Table 3

Quantities of C_3H_6 formed (in millitorr in a 210cm^3 reactor), as a function of pyrolysis time (second).

T = 925K

		Time (second)					
		18	30	45	60	90	120
C_2H_4	CH_4	C_3H_6 (millitorr)					
25	0	7.4	21 20	42	60		
25	100	22	51	88	121	220	
25	400		56		108		259

		Time (second)				
		30	60	90	120	180
C_2H_4	CH_4	C_3H_6 (millitorr)				
12.5	0	5.3	15 14	25	36	
12.5	50	15	36		82	134
12.5	200	15	32		71	113

Table 4

Quantities of 1-C_4H_8 formed (in millitorr in a 210cm^3 reactor), as a function of pyrolysis time (second).
T = 925K

		Time (second)					
		18	30	45	60	90	120
C_2H_4	CH_4	1-C_4H_8 (millitorr)					
25	0	6.2	10 10	12	13		
25	100	0.7	1.7	2.6	3.8	5.3	
25	400		0.4		0.8		2.0

		Time (second)				
		30	60	90	120	180
C_2H_4	CH_4	1-C_4H_8 (millitorr)				
12.5	0	2.6	3.7 3.4	5.9	8.5	
12.5	50	0.2	0.5		1.1	1.5
12.5	200	<0.2	0.2		0.3	

Table 5

Quantities of 1,3-C_4H_6 formed (in millitorr in a 210cm^3 reactor), as a function of pyrolysis time (second).

T = 925K

		Time (second)					
		18	30	45	60	90	120
C_2H_4	CH_4	1,3-C_4H_6 (millitorr)					
25	0	35	81 77	131	165		
25	100	14	31	54	73	122	
25	400		16		33		77

		Time (second)				
		30	60	90	120	180
C_2H_4	CH_4	1,3-C_4H_6 (millitorr)				
12.5	0	35	73 71	105	133	
12.5	50	8.7	22		50	80
12.5	200	4.8	10		22	34

Table 6

Quantities of C_2H_6 formed (in millitorr in a 210cm^3 reactor), as a function of pyrolysis time (second).
T = 974K

		Time (second)					
		18	30	45	60	90	120
C_2H_4	CH_4	C_2H_6 (millitorr)					
12.5	0	9.9	18	24	30	45	
12.5	50	2.8*	6.5		16		43
12.5	200		4.8		11	22	33
					11		

		Time (second)					
		30	60	90	120	180	240
C_2H_4	CH_4	C_2H_6 (millitorr)					
6.25	0	3.9**	7.0	9.0	11	15	
			6.6				
6.25	25	1.2	2.9		7.6		19
6.25	100	1.0	2.3		6.3	12	

* 19 seconds instead of 18.
** 32 seconds instead of 30.

Table 7

Quantities of C_2H_2 formed (in millitorr in a 210cm^3 reactor), as a function of pyrolysis time (second).

T = 974K

		Time (second)					
		18	30	45	60	90	120
C_2H_4	CH_4	C_2H_2 (millitorr)					
12.5	0	9.7	20	30	38	63	
12.5	50	1.9*	4.4		11		30
12.5	200		3.4		7.5	14	21
					7.2		

		Time (second)					
		30	60	90	120	180	240
C_2H_4	CH_4	C_2H_2 (millitorr)					
6.25	0	8.1**	17	25	33	46	
			16				
6.25	25	1.4	3.5		9.8		26
6.25	100	1.4	2.9		7.7	14	

* 19 seconds instead of 18.
** 32 seconds instead of 30.

Table 8

Quantities of C_3H_6 formed (in millitorr in a 210cm^3 reactor), as a function of pyrolysis time (second).

T = 974K

		Time (second)					
		18	30	45	60	90	120
C_2H_4	CH_4	C_3H_6 (millitorr)					
12.5	0	13	27	39	49	74	
12.5	50	34*	72		158		429
12.5	200		68		144	254	354
					137		

		Time (second)					
		30	60	90	120	180	240
C_2H_4	CH_4	C_3H_6 (millitorr)					
6.25	0	6.8**	14	19	23	29	
			13				
6.25	25	32	67		115		202
6.25	100	25	51		121	203	

* 19 seconds instead of 18.
** 32 seconds instead of 30.

Table 9

Quantities of 1,3-C_4H_6 formed (in millitorr in a 210cm^3 reactor), as a function of pyrolysis time (second).

T = 974K

		Time (second)					
		18	30	45	60	90	120
C_2H_4	CH_4	1,3-C_4H_6 (millitorr)					
12.5	0	116	188	236	257	321	
12.5	50	22*	46		102		199
12.5	200		19		41	69	99
					40		

		Time (second)					
		30	60	90	120	180	240
C_2H_4	CH_4	1,3-C_4H_6 (millitorr)					
6.25	0	78**	126	138	153	158	
			120				
6.25	25	14	32		72		124
6.25	100	7.2	14		34	55	

* 19 seconds instead of 18.
** 32 seconds instead of 30.

Table 10

Quantities of C_2H_6 formed (in millitorr in a 210cm^3 reactor),
as a function of pyrolysis time (second).
T = 1023K

		Time (second)						
		12.5	18	30	45	60	90	
C_2H_4	CH_4	C_2H_6 (millitorr)						
12.5	0	15	23*	30	35**	45		
12.5	50		11	22	40	59		
12.5	200		9.1#	20		66	113	

		Time (second)						
		21	30	46	60	90	120	180
C_2H_4	CH_4	C_2H_6 (millitorr)						
6.25	0	5.1	6.0	8.7	9.9	13	15	
6.25	25		5.0		13	22	29	37
6.25	100		5.1		17		47	71

* 20 seconds instead of 18.
** 40 seconds instead of 45.
# 19 seconds instead of 18.

Table 11

Quantities of C_2H_2 formed (in millitorr in a 210cm^3 reactor), as a function of pyrolysis time (second).

T = 1023K

		Time (second)						
		12.5	18	30	45	60	90	
C_2H_4	CH_4	C_2H_2 (millitorr)						
12.5	0	58	96*	130	159**	205		
12.5	50		22	43	78	110		
12.5	200		16#	33		90	133	

		Time (second)						
		21	30	46	60	90	120	180
C_2H_4	CH_4	C_2H_2 (millitorr)						
6.25	0	39	50	80	92	127	148	
6.25	25		15		41	75	100	132
6.25	100		13		35		87	125

* 20 seconds instead of 18.
** 40 seconds instead of 45.
\# 19 seconds instead of 18.

Table 12

Quantities of C_3H_6 formed (in millitorr in a 210cm^3 reactor), as a function of pyrolysis time (second).

T = 1023K

		Time (second)						
		12.5	18	30	45	60	90	
C_2H_4	CH_4	C_3H_6 (millitorr)						
12.5	0	33	49*	60	65**	67		
12.5	50		180	302	422	475		
12.5	200		175#	337		726	852	

		Time (second)						
		21	30	46	60	90	120	180
C_2H_4	CH_4	C_3H_6 (millitorr)						
6.25	0	16	19	26	26	27	25	
6.25	25		111		201	251	243	198
6.25	100		122		278		452	444

* 20 seconds instead of 18.
** 40 seconds instead of 45.
# 19 seconds instead of 18.

Table 13

Quantities of 1,3-C_4H_6 formed (in millitorr in a 210cm^3 reactor), as a function of pyrolysis time (second).

T = 1023K

		Time (second)						
		12.5	18	30	45	60	90	
C_2H_4	CH_4	1,3-C_4H_6 (millitorr)						
12.5	0	274	322*	351	347**	346		
12.5	50		109	184	251	283		
12.5	200		46#	85		175	199	

		Time (second)						
		21	30	46	60	90	120	180
C_2H_4	CH_4	1,3-C_4H_6 (millitorr)						
6.25	0	156	160	179	171	164	148	
6.25	25		66		124	149	150	123
6.25	100		30		67		109	105

* 20 seconds instead of 18.
** 40 seconds instead of 45.
\# 19 seconds instead of 18.

Table 14

Quantities of products formed (in millitorr in a 210cm^3 reactor)
and of C_2H_4 remaining (Torr), as a function of pyrolysis time (second).
Initial mixture, C_2H_4 (6.5 Torr) - CH_4 (356 Torr)
T = 974K

Time	60	120	240	300	360	480	600	840	1200	1800
C_2H_4	6.38 6.44	6.51 6.43 6.25	6.26 6.25 6.05	5.96	5.93 5.85	5.55 5.60	5.30	4.82	4.08	3.61
C_2H_6	4.0 3.3	8.7 8.8 7.6	21 19 21	29	40 54	71 73	84	109	155	179
C_2H_2	3.7 3.4	8.1 8.2 7.1	18 16 17	21	29 34	42 45	48	53	57	50
C_3H_6	74 71	157 157 137	316 296 309	373	488 559	644 673	683	706	618	444
C_3H_4	0.1 0.1	0.7 0.7 0.5	3.2 2.8 3.0	4.5	7.5 9.5	13 14	14	16	14	10
1-C_4H_8	0.1 0.1	0.3 0.3 0.2	0.8 0.8 0.9	1.3	2.2 2.8	3.7 4.1	4.3 4.5	4.5	4.7	3.4
1,3-C_4H_6	7.0 6.5	15 15 13	30 28 29	39	48 56	69 70	74	80	73	52
2-C_4H_8	0.2 0.2	0.5 0.5 0.5	1.3 1.2 1.2	1.9	2.8 3.5	3.1 4.6	4.9	4.7	4.3	3.2
C_5	0.0 0.0	0.0 0.0 0.0	4.8 3.6 4.3	6.9	11 14	19 22	24	26	42	17
C_6	0.0 0.0	0.4 0.3 0.2	 1.2 1.2	2.3	6.1 10	22 20	32	67	162	247
C_7	0.0 0.0	0.0 0.0 0.0	0.0 0.0 0.0	0.0	0.1 0.1	0.4 0.7		4.2	12	15
Total C produced (Torr)	0.27 0.25	0.57 0.57 0.50	1.20 1.11 1.17	1.45	1.94 2.27	2.73 2.85	3.02	3.41	3.92	3.74

Table 15

Quantities of products formed (in millitorr in a 210cm^3 reactor)
and of C_2H_4 remaining (Torr), as a function of pyrolysis time (second).
Initial mixture, C_2H_4 (6.5 Torr) - CH_4 (356 Torr)
T = 1023K

Time	30	60	120	120	240	360	480	600	720	900
C_2H_4	6.52	6.07 6.20	5.99 6.00	5.81	5.35 5.12 5.14	4.47 4.48	4.13	3.73	3.52	3.49
C_2H_6	8.1 9.0 6.3	23 18 15	60 60 51	63	148 112 141	165 160	156 174		176	191
C_2H_2	11 12 9.8	28 25 22	62 63 57	64	121 96 116	117 116	99	100	96	94
C_3H_6	128 135 111	287 258 230	551 558 515	564	670 578 660	520 517	383	345	311	275
C_3H_4	1.0 1.0	5.1 4.0 3.1	20 20 18	19	33 29 33	26 26	19	17	15	12
1-C_4H_8	0.1 0.1	0.5 0.4 0.3	2.1 2.1 1.8	2.4	4.2 3.4 3.8	3.1 3.6	2.8	2.4	1.9	1.6
1,3-C_4H_6	11 12 10	26 22 20	55 55 50	57	83 73 85	67 70	50	43	36	30
2-C_4H_8	0.3 0.3	1.1 0.7	3.1 2.9	2.7	4.2 4.2 4.5	3.5 3.6	2.8	2.4	1.6	1.3
C_5	1.1 0.8	7.1 5.7	32 32		51 46 53	43 45		28	24	14
C_6	0.1 0.1	0.7 0.6	9.4 9.9		98 97	194		337	381	381
C_7	0.0 0.0	0.0 0.0	0.2 0.3		4.8 10	14		33	20	17
Total C (Torr)	0.52 0.50	1.13 0.99	2.41 2.44		3.89 3.89	3.98		4.17	4.23	4.04

Table 16